



ANNUAL REPORTS  
ON THE  
PROGRESS OF CHEMISTRY.





# ANNUAL REPORTS

ON THE

## PROGRESS OF CHEMISTRY

### FOR 1922

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## TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>A.</i> . . . . .	Abstracts in Journal of the Chemical Society.*
<i>Amer. Chem. J.</i> . . . . .	American Chemical Journal.
<i>Amer. J. Bot.</i> . . . . .	American Journal of Botany.
<i>Amer. J. Dis. Child.</i> . . . . .	American Journal of Diseases of Children.
<i>Amer. J. Hygiene</i> . . . . .	American Journal of Hygiene.
<i>Amer. J. Physiol.</i> . . . . .	American Journal of Physiology.
<i>Amer. J. Sci.</i> . . . . .	American Journal of Science.
<i>Amer. Min.</i> . . . . .	American Mineralogist.
<i>Anal. Assoc. Quím. Argentina</i>	Anales de la Asociación Química Argentina.
<i>Anal. Fis. Quím.</i> . . . . .	Anales de la Sociedad Española Física y Química.
<i>Analyst</i> . . . . .	The Analyst.
<i>Annalen</i> . . . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Appl. Biol.</i> . . . . .	Annals of Applied Biology.
<i>Ann. Bot.</i> . . . . .	Annals of Botany.
<i>Ann. Chim. anal.</i> . . . . .	Annales de Chimie analytique appliquée à l'Industries à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Physik</i> . . . . .	Annalen der Physik.
<i>Ann. Phytopath. Soc. Japan.</i>	Annals of the Phytopathic Society, Japan.
<i>Ann. Report</i> . . . . .	Annual Reports of the Chemical Society.
<i>Arch. exp. Path. Pharm.</i> . . . . .	Archiv für experimentelle Pathologie und Pharma- kologie.
<i>Arch. Farm. sperim. Sci.</i> . . . . .	Archivio di Farmacologia sperimentale e Scienze affini.
<i>Arch. Pharm.</i> . . . . .	Archiv der Pharmazie.
<i>Arch. Schiffs u. Tropenhygiene</i>	Archiv Schiffs-und Tropen-Hygiene.
<i>Arch. Suikerindus. Ned. Ind.</i>	Archiv voor de Suikerindustrie in Nederlandsch-Indie.
<i>Arkiv. Kem. Min. Geol.</i> . . . . .	Arkiv för Kemi, Mineralogi och Geologi.
<i>Astrophys. J.</i> . . . . .	Astrophysical Journal.
<i>Atti R. Accad. Lincei</i> . . . . .	Atti della Reale Accademia Nazionale dei Lincei.
<i>Ber.</i> . . . . .	Berichte der Deutschen Chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i> . . . . .	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i> . . . . .	Berichte der Deutschen pharmazeutischen Gesell- schaft.
<i>Berl. Klin. Wochenschr.</i> . . . . .	Berliner Klinische Wochenschrift.
<i>Bied. Zentr.</i> . . . . .	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
<i>Biochem. J.</i> . . . . .	The Biochemical Journal.
<i>Biochem. Z.</i> . . . . .	Biochemische Zeitschrift.
<i>Boll. Chim. farm.</i> . . . . .	Bolletino Chimico farmaceutico.
<i>Brennstoff-Chem.</i> . . . . .	Brennstoff Chemie.
<i>Brit. Assoc. Rep.</i> . . . . .	Report of the British Association for the Advance- ment of Science.
<i>Brit. Med. J.</i> . . . . .	British Medical Journal.
<i>Brit. Pat.</i> . . . . .	British Patent.
<i>Bul. Soc. Chim. România</i>	Buletinul Societății de Chimie din România.
<i>Bull. Acad. Sci. Cracovie</i> . . . . .	Bulletin International-Académie des Sciences de Cracovie.

\* The year is not inserted in references to 1922.

viii TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Bull. Bur. Biotechn.</i> . . .	Bulletin of the Bureau of Biotechnology.
<i>Bull. Johns Hopkins Hosp.</i> . . .	Bulletin of the Johns Hopkins Hospital.
<i>Bull. Sci. Pharmacol.</i> . . .	Bulletin des Sciences Pharmacologiques.
<i>Bull. Soc. chim.</i> . . .	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i> . . .	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. chim. Biol.</i> . . .	Bulletin de la Société de Chimie biologique.
<i>Canada Med. Assoc. J.</i> . . .	Journal of the Canadian Medical Association.
<i>Chem. Listy</i> . . .	Chemické Listy pro Vědu a Průmysl.
<i>Chem. and Met. Eng.</i> . . .	Chemical and Metallurgical Engineering.
<i>Chem. News</i> . . .	Chemical News.
<i>Chem. Weekblad</i> . . .	Chemisch Weekblad.
<i>Chem. Ztg.</i> . . .	Chemiker Zeitung.
<i>Chem. Zentr.</i> . . .	Chemisches Zentralblatt.
<i>Chim. et Ind.</i> . . .	Chimie et Industrie.
<i>Compt. rend.</i> . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Compt. rend. Soc. Biol.</i> . . .	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
<i>D. R.-P.</i> . . .	Deutsches Reichs-Patent.
<i>Fermentforsch.</i> . . .	Fermentforschung.
<i>Gazzetta</i> . . .	Gazzetta chimica italiana.
<i>Geol. For. Forh.</i> . . .	Geologiska Föreningens i Stockholm Förhandlingar.
<i>Giorn. Chim. Ind. Appl.</i> . . .	(Giornale di Chimica Industriale ed Applicata.
<i>Helv. Chim. Acta</i> . . .	Helvetica Chimica Acta.
<i>Internat. Mitt. Bodenkunde</i> . . .	Internationale Mitteilungen für Bodenkunde.
<i>J. Agric. Res.</i> . . .	Journal of Agricultural Research.
<i>J. Agric. Sci.</i> . . .	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i> . . .	Journal of the American Chemical Society.
<i>J. Amer. Med. Assoc.</i> . . .	Journal of the American Medical Association.
<i>J. Assoc. Off. Agr. Chem.</i> . . .	Journal of the Association of Official Agricultural Chemists.
<i>J. Bact.</i> . . .	Journal of Bacteriology.
<i>J. Biochem. (Japan)</i> . . .	Journal of Biochemistry (Japan).
<i>J. Biol. Chem.</i> . . .	Journal of Biological Chemistry.
<i>J. Chem. Ind. Japan (or Tokyo)</i> . . .	Journal of Chemical Industry, Japan.
<i>J. Chem. Soc. Japan.</i> . . .	Journal of the Chemical Society of Japan.
<i>J. Chim. phys.</i> . . .	Journal de Chimie physique.
<i>J. Coll. Agric. Hokaido</i> . . .	Journal of the College of Agriculture, Hokaido.
<i>J. Exper. Med.</i> . . .	Journal of Experimental Medicine.
<i>J. Franklin Inst.</i> . . .	Journal of the Franklin Institute.
<i>J. Gen. Physiol.</i> . . .	Journal of General Physiology.
<i>J. Ind. Eng. Chem.</i> . . .	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Brewing</i> . . .	Journal of the Institute of Brewing.
<i>J. Landw.</i> . . .	Journal für Landwirtschaft.
<i>J. Min. Agric.</i> . . .	Journal of the Ministry of Agriculture.
<i>J. Opt. Soc. Amer.</i> . . .	Journal of the Optical Society of America.
<i>J. Pharm. Chim.</i> . . .	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Soc. Japan.</i> . . .	Journal of the Pharmaceutical Society of Japan.
<i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Phys. Radium</i> . . .	Journal de Physique et le Radium.
<i>J. Physiol.</i> . . .	Journal of Physiology.
<i>J. pr. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i> . . .	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i> . . .	Journal of the Society of Chemical Industry.
<i>J. Washington Acad. Sci.</i> . . .	Journal of the Washington Academy of Sciences.
<i>Kentucky Exp. Sta. Bul.</i> . . .	Kentucky Experimental Station Bulletin.
<i>Koll. Chem. Beihefte</i> . . .	Kolloidchemische Beihefte.
<i>Kolloid Z.</i> . . .	Kolloid Zeitschrift.
<i>Landw. Jahrb.</i> . . .	Landwirtschaftliche Jahrbücher.

# TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES. ix

ABBREVIATED TITLE	JOURNAL.
<i>Landw. Versuchs-Stat.</i>	Die Landwirtschaftlichen Versuchs-Stationen.
<i>Medd. K. Vetenskapsakad.</i>	Meddelanden från Kongl-Vetenskapsakademiens
<i>Nobel-Inst.</i>	Nobel-Institut.
<i>Mem. Manchester Phil. Soc.</i>	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Michigan Agric. Exp. Sta.</i>	Michigan Experimental Station Bulletin.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Mon. Sci.</i>	Moniteur Scientifique.
<i>Nachr. Ges. Wiss. Göttingen</i>	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
<i>Naturwiss.</i>	Die Naturwissenschaften.
<i>Oesterr. Chem. Ztg.</i>	Oesterreichische Chemiker-Zeitung.
<i>Oregon Agric. Exp. Sta. Bull.</i>	Oregon Experimental Station Bulletin.
<i>P.</i>	Proceedings of the Chemical Society.
<i>Pharm. Weekblad</i>	Pharmaceutisch Weekblad.
<i>Pharm. Zentr.-h.</i>	Pharmazeutische Zentralhalle.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Physical Rev.</i>	Physical Review.
<i>Physikal. Z.</i>	Physikalische Zeitschrift.
<i>Proc. Amer. Phil. Soc.</i>	Proceedings of the American Philosophical Society.
<i>Proc. Cam. Phil. Soc.</i>	Proceedings of the Cambridge Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Nat. Acad. Sci.</i>	Proceedings of the National Academy of Sciences.
<i>Proc. Physical Soc.</i>	Proceedings of the Physical Society of London.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Proc. Soc. Exp. Biol. Med.</i>	Proceedings of the Society of Experimental Biology and Medicine.
<i>Rec. trav. chim.</i>	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rev. Mét.</i>	Revue de Métallurgie.
<i>Schweiz. Apoth. Ztg.</i>	Schweizerische Apotheker Zeitung.
<i>Sci. Proc. R. Dublin Soc.</i>	Scientific Proceedings of the Royal Dublin Society.
<i>Sitzungsber. Akad. Wiss. Wien</i>	Sitzungsberichte der Akademie der Wissenschaften Wien.
<i>Sitzungsber. Preuss. Akad. Wiss. Berlin</i>	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
<i>Skand. Arch. Physiol.</i>	Skandinavisches Archiv für Physiologie.
<i>Soil Sci.</i>	Soil Science.
<i>Svensk. Kem. Tidskr.</i>	Svensk Kemist Tidskrift.
<i>T.</i>	Transactions of the Chemical Society.
<i>Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>Trans. Roy. Soc. Canada</i>	Transactions of the Royal Society of Canada.
<i>U. S. Geol. Survey Prof. Paper</i>	United States Geological Survey Professional Paper.
<i>U. S. Pat.</i>	United States Patent.
<i>Ver. Deut. Physikal. Ges.</i>	Verhandlungen der deutschen physikalischen Gesellschaft.
<i>Wiss. Veröffentl. Siemens Konzern</i>	Wissenschaftliche Veröffentlichungen aus dem Siemens Konzern.
<i>Z. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Z. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Z. anorg. Chem.</i>	Zeitschrift für anorganische und allgemeine Chemie.
<i>Z. Biol.</i>	Zeitschrift für Biologie.
<i>Z. Elektrochem.</i>	Zeitschrift für Elektrochemie.



X TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Z. ges. Schiess- u. Sprengstoffw.</i> . . . .	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
<i>Z. Hyg.</i> . . . .	Zeitschrift für Hygiene und Infektionskrankheiten.
<i>Z. Metallk.</i> . . . .	Zeitschrift für Metallkunde.
<i>Z. Nahr.-Genussm.</i> . . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Z. Physik</i> . . . .	Zeitschrift für Physik.
<i>Z. physikal. Chem.</i> . . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Z. physikal. Chem. Unterr.</i>	Zeitschrift für den physikalischen und Chemischen Unterricht.
<i>Z. physiol. Chem.</i> . . . .	Hoppe-Sevler's Zeitschrift für physiologische Chemie.
<i>Z. wiss. Photochem.</i> . . . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.

# ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY.

## GENERAL AND PHYSICAL CHEMISTRY.

### *Spectra of Hydrogen and Helium.*

THE line spectrum attributed to neutral helium contains 105 lines, forty of which are accounted for by a formula<sup>1</sup> derived on the assumption that the mutual perturbation of the electrons is negligible. It is anticipated that the majority of the remaining lines will be found to fit the formula, and the conclusion is drawn that the field of force of the bound electrons is entirely engaged by the nucleus. In a criticism<sup>2</sup> of this interpretation of the spectrum, it is suggested that the agreement between the observed and calculated frequencies is largely fortuitous.

The band spectrum of helium has been further investigated.<sup>3</sup> Fowler found that the heads of some of the bands in this spectrum conform to the ordinary law for line series. It is now shown that three of the remaining bands, including the strongest in the spectrum, can be deduced from the recently developed quantum theory of band spectra. The three bands in question are supposed to be emitted by a molecule which is undergoing simultaneous changes in its rotational and internal energies, and, in agreement with theory, each band contains three main series of lines represented by similar parabolic formulæ and characterised by a common fundamental frequency which is not simply related to the "head" of the band. This work is of general interest on account of the support it affords to the view that diatomic molecules of helium exist under the conditions which prevail in the discharge tube.

Although the origin of some parts of the secondary spectrum of hydrogen is probably analogous to that of the helium bands, its structure is still obscure. Electric discharge through vacuum tubes is the only known means by which this spectrum is excited

<sup>1</sup> L. Silberstein, *Nature*, 1922, **110**, 247; *A.*, ii, 674.

<sup>2</sup> C. V. Raman, *ibid.*, 700; *A.*, ii, 803.

<sup>3</sup> W. E. Curtis, *Proc. Roy. Soc.*, 1922, [A], **101**, 38; *A.*, ii, 330.

and its intensity, relative to that of the Balmer lines, increases with the purity of the hydrogen. The Doppler effect, to which the spectral broadening of monochromatic radiation is to be attributed, affords a means of determining the mass of the radiating particle with the aid of Rayleigh's formula,  $\alpha_\lambda = k\lambda\sqrt{T/M}$ , in which  $\alpha_\lambda$  is the half-width of the line of wave-length  $\lambda$ ,  $M$  is the mass of the radiator, and  $T$  the absolute temperature. The older methods of determining the "half-width" fail to give satisfactory results in dealing with such closely packed lines as those in the secondary spectrum of hydrogen, of which 1200 have been measured at an average interval of less than 3 Å. A new method<sup>4</sup> has, however, been described which depends on the relation between the width of the photographic image of the line under investigation and the intensity of the radiating source. If the intensity is cut down to a known fraction, whilst the time of exposure remains the same, it can be shown that for an apparatus of given dispersive power, the difference between the widths of the images is determined by the "half-width" of the line examined. Such "half-width" data indicate definitely that the hydrogen molecule is the source of the secondary spectrum of hydrogen. The same conclusion has been reached by R. W. Wood,<sup>5</sup> who, by eliminating the secondary spectrum and the faint continuous background, and by the use of long exposures, has increased the number of observed Balmer lines to twenty.

#### *Fluorescence of Mercury Vapour.*

The fluorescence of mercury vapour is only exhibited<sup>6</sup> when the vapour has been freshly distilled from liquid mercury at temperatures above 150°. It is suggested that such vapour contains aggregates of mercury atoms as well as the normal monatomic molecules and that the former are responsible for the fluorescence. The continuous portion of the fluorescence spectrum has also been produced<sup>7</sup> by the electrical excitation of mercury vapour. The spectrum is only obtained within certain limiting temperatures and when the density of the exciting current is low.

#### *Specific Heats of Gases.*

Although the advances recently made in the interpretation of the specific heats of solids involve the acceptance of views which

<sup>4</sup> T. R. Merton and S. Barratt, *Phil. Trans.*, 1922, [A], 222, 369; *A.*, ii, 461.

<sup>5</sup> *Phil. Mag.*, 1922, [vi], 44, 538; *A.*, ii, 673.

<sup>6</sup> J. S. van der Linden and R. W. Wood, *Astrophys. J.*, 1921, 54, 148; *A.*, ii, 245.

<sup>7</sup> C. D. Child, *ibid.*, 1922, 55, 329; *A.*, ii, 676.

are incompatible with the equipartition principle, there is an evident disinclination to discard this principle in the theoretical treatment of the specific heats of gases.

As the simplest member of the group of polyatomic gases, the behaviour of hydrogen is of peculiar interest in this connexion. At very low temperatures, its specific heat is constant and it behaves as a monatomic gas. At higher temperatures, the specific heat increases with the temperature, but the relation between the heat capacity and the temperature is not of a simple kind.

On the assumption that collisions between the gaseous molecules give rise to additional degrees of freedom when the velocities of the colliding molecules exceed a certain critical value, the total energy of the gas will be the sum of the energies of the fraction for which the collision velocities are less than the critical value, and of the fraction for which the velocities of collision are greater than this. By assigning an appropriate value to the critical velocity, and assuming that the molecules in the two groups have three and five degrees of freedom, respectively, it has been shown<sup>8</sup> that the observed variation in the molecular heat of hydrogen at temperatures below 0° can be accounted for in a fairly satisfactory manner.

Bjerrum, Krüger, and Eucken had previously shown that the quantum theory affords a promising basis for the interpretation of the experimental data, although the formulæ suggested by these authors show deviations from the observed numbers which are greater than the errors of experiment.

A more recent investigation<sup>9</sup> of the problem shows that the entire range of data can be represented very satisfactorily by the formula

$$C_v = \frac{3}{2}R + 1.13Rf(\nu_1) + RF(\nu_2),$$

in which  $R$  is the gas constant,  $f$  and  $F$  are abbreviations for the Planck-Einstein and the Nernst-Lindemann functions, respectively, and  $\nu_1 = 10.06 \times 10^{12}$ ,  $\nu_2 = 1.84 \times 10^{14}$  are characteristic rotation and vibration frequencies calculated from numerical data relating to Bohr's model of the hydrogen molecule. The first term gives the energy increment per degree at low temperatures and has reference solely to translational energy; since the corresponding quanta are very small, the energy exchange is practically continuous and in agreement with the equipartition theory. Above 60° abs., the influence of the rotational quanta, represented by the second term, begins to be appreciable and causes  $C_v$  to rise to about  $\frac{5}{2}R$ , at which point the vibration quantum comes into play and

<sup>8</sup> G. W. Todd, *Phil. Mag.*, 1920, [vi], 40, 357; *A.*, 1920, ii, 585.

<sup>9</sup> C. K. Ingold and (Miss) E. H. Usherwood, *T.*, 1922, 121, 2286.

causes a further rise in the molecular heat as the temperature increases. The introduction of the factor 1.13 in the second term represents an empirical adjustment, in regard to which it is tentatively suggested that the quantity  $0.13Rf(\nu_1)$  may correspond with some form of potential energy which is associated with precessional motion.

In reproducing the experimental data, the above formula is a distinct improvement on that proposed by F. H. MacDougall,<sup>10</sup> who also employs Bohr model frequencies but, on the other hand, assumes that the hydrogen molecule has three degrees of rotational freedom and uses Planck-Einstein functions in evaluating the rotational and vibrational energy terms.

The successful application of the notions associated with the quantum theory in so many different directions leads rather naturally to the expectation that this will ultimately provide the key to the theoretical treatment of the problem of the energies of gaseous molecules, but so long as the agreement between theory and experiment depends in the first instance on the arbitrary choice of the number of the degrees of freedom and of the nature of the operating functions, and subsequently on the empirical adjustment of the formulæ so derived, it is perhaps not difficult to understand why there should be a certain reluctance to ignore the equipartition principle in dealing with this problem.

With the object of providing accurate data for the theoretical investigation of the problem, an improved adiabatic method has been developed<sup>11</sup> for the determination of the specific heat ratio, and measurements<sup>12</sup> have been made of the specific heats of a number of gases.

The specific heat of a gas has an abnormally high value if with rise of temperature it dissociates or undergoes some intramolecular change which is accompanied by heat absorption. The value of the molecular heat ratio  $\gamma = (C_p + R)/C_p$  will under these circumstances be less than the normal value. These considerations have been applied<sup>13</sup> to detect and measure the supposed tautomeric equilibrium represented by  $\text{HCN} \rightleftharpoons \text{HNC}$  in gaseous hydrogen cyanide. The heat absorbed in the transformation of formonitrile into carbylamine is about 7000 calories per gram-molecule, a value large enough to ensure the detection of the

<sup>10</sup> *J. Amer. Chem. Soc.*, 1921, **43**, 23; *A.*, 1921, ii, 238; see also *Ann. Rep.*, 1921, 1.

<sup>11</sup> J. R. Partington, *Proc. Roy. Soc.*, 1921, [A], **100**, 27; *A.*, 1921, ii, 621.

<sup>12</sup> J. R. Partington and H. J. Cant, *Phil. Mag.*, 1922, [vi], **43**, 369; *A.*, ii, 191.

<sup>13</sup> (Miss) E. H. Usherwood, *T.*, 1922, **121**, 1604.

tautomeric equilibrium, even if one of the tautomeric forms is present at the temperature of the measurements only in very small proportion. The experimental data actually show that gaseous hydrogen cyanide is a mixture consisting mainly of HCN in equilibrium with a small amount (not more than a few tenths of one per cent.) of the isomeric form, HNC.

*Viscosity of Gases and Molecular Configuration.*

Measurements of the viscosity of gases provide data which would appear to throw some light on the arrangement of the atoms in the molecules of which they form part.

The viscosity depends on the frequency of molecular collisions, which in its turn is determined by the effective cross-sectional areas which are presented by the molecules as targets. The average area presented by a molecule in all possible orientations is known as the "mean collision area" and this is calculated from the viscosity in the same way as the cross-sectional area of a molecule which is assumed to be spherical.

When such "mean collision areas" are considered<sup>14</sup> in reference to modern views of atomic structure, and to the part which, according to the Lewis-Langmuir theory, is played by the valency electrons in the combination of the elements to form compounds, it is apparent that this magnitude will depend on the molecular configuration.

It seems natural to suppose that elements which have the same number of electron rings and which differ only in regard to the degree of development of the outermost ring will show comparatively slight variations in atomic diameter, provided of course that the number of such valency electrons is not too small. Contiguous elements on the right-hand side of the periodic table form such a group. It has in fact been shown<sup>15</sup> by X-ray measurements that the domains occupied by the atoms of such contiguous elements are the same within narrow limits, and other evidence<sup>16</sup> pointing in the same direction is available.

According to the Lewis-Langmuir theory, the hydrogen compounds of the elements chlorine, sulphur, phosphorus, and silicon<sup>17</sup> have an outer ring structure which is essentially identical with the outer ring structure of the inert element argon. The outer rings of these elements are indeed completed by the entry of one, two, three, and four electrons, respectively, from the corresponding

<sup>14</sup> A. O. Rankine, *Trans. Faraday Soc.*, 1922, **17**, 719; *A.*, ii, 635.

<sup>15</sup> W. L. Bragg, *Phil. Mag.*, 1920, [vi], **40**, 169; *A.*, 1920, ii, 537.

<sup>16</sup> A. O. Rankine, *Proc. Roy. Soc.*, 1921, [A], **98**, 360; *A.*, 1921, ii, 192.

<sup>17</sup> A. O. Rankine and C. J. Smith, *Proc. Phys. Soc.*, 1922, **34**, 181; *A.*, ii, 709.

number of hydrogen atoms. Differences in size and shape may therefore be attributed to the hydrogen nuclei which are associated with these electrons in the respective hydrogen compounds.

The "mean collision areas" of such compounds compared with that of argon are shown in the following series :

	A.	HCl.	H <sub>2</sub> S.	PH <sub>3</sub> .	SiH <sub>4</sub> .
Mean collision area .....	1.00	1.04	1.19	1.41	1.53
Difference .....		0.04	0.15	0.22	0.12

On the assumption that the hydrogen nuclei may be regarded as forming protuberances on the spherical argon atom, the above data point to the conclusion that the distance between the hydrogen nuclei and the nucleus of the central atom increases with increase in the number of hydrogen atoms in the molecule. The reason for this is possibly to be found in the mutual repulsion of the hydrogen nuclei.

The difference figures show that the increase in the "mean collision area" due to a hydrogen nucleus reaches a maximum when the third nucleus is attached, the effect of the fourth being distinctly smaller. It is to be noted, however, that in the case of phosphine, and still more in the case of silicane, the effect of the repulsion will be to some extent obscured, in so far as the viscosity is concerned, by the overlapping of the nuclear prominences which occur in certain orientations of the molecule.

The viscosity data for other groups of related compounds have also been interpreted<sup>18</sup> in the light of the Lewis-Langmuir theory. According to this, the molecule of carbon dioxide is externally equivalent to three linked atoms of neon with their centres disposed linearly. If one of the external neon atoms is replaced by an atom of argon, an electronic configuration is obtained which is equivalent to that of carbon oxysulphide. The "mean collision areas" calculated from the viscosities of carbon dioxide and carbon oxysulphide are in good agreement with this view of their molecular structure.

#### *Limiting Densities of Gases.*

The compressibilities of oxygen, hydrogen, carbon dioxide,<sup>19</sup> and ethylene<sup>20</sup> have been measured at low pressures. The values of  $(pv)_0/(pv)_1$  lead to the following values for the atomic weights : H = 1.0077, C = 11.998 (from carbon dioxide), C = 12.000 (from ethylene).

Wohl's equation of condition has been applied<sup>21</sup> to the deter-

<sup>18</sup> A. O. Rankine, *Phil. Mag.*, 1922, [vi], **44**, 292; *A.*, ii, 704.

<sup>19</sup> P. A. Guye and T. Batuecas, *Helv. Chim. Acta*, 1922, **5**, 532; *A.*, ii, 617.

<sup>20</sup> T. Batuecas, *ibid.*, 544; *A.*, ii, 618.

<sup>21</sup> *Z. physikal. Chem.*, 1921, **99**, 207; *A.*, ii, 117.

mination of the limiting density ( $D_0$ ) of a number of gases, the relation between this and the normal density ( $D$ ) being given by the equation  $D_0/D = 1 + \frac{t}{15p_c} (1 - 6.4t^2)$ , where  $t = T_c/T$  and  $p_c$  is the critical pressure. The molecular weights corresponding with the limiting densities are in close agreement with those derived from the formula of D. Berthelot, which is of the same form as that given above and differs from it only in the values of the numerical constants involved.

### *Equations of Condition.*

Attention has been recently directed to the exactitude with which the observed relations between the pressure, volume, and temperature of fluids are reproduced by the equation of A. Wohl.<sup>21a</sup> This equation may be written in the form,

$$p = \frac{RT}{v-b} - \frac{a}{Tv(v-b)} + \frac{c}{T^2v^3},$$

in which the second term on the right represents the diminution of pressure due to the attractive forces and the third term represents the increase due to the repulsive forces which come into play at high pressures as a result of the rotational movements of the molecules.

The equation is of the fourth degree in regard to  $v$  and apparently contains four constants, but on the assumption that the four roots are identical in the critical condition, it may be shown that the four constants can be expressed in terms of the critical data, or, more conveniently from the experimental point of view, in terms of the specific constants  $p_c$  and  $T_c$ , and the general constant  $R$ . Since three independent constants only are involved, the Wohl equation can be transformed into a general reduced equation of condition.

In comparing the Wohl equation with that of van der Waals, it should be noted that although the latter expresses qualitatively the relations between the gaseous and liquid states, it can only be regarded as a very approximate quantitative statement of the behaviour of fluids. Wohl's equation, however, represents the experimental results with very considerable accuracy over an extended range. Furthermore, this equation reproduces the experimental values of  $v_c$  and  $\frac{RT_c}{p_c v_c}$ , and since at low pressures it is practically identical with the equation of D. Berthelot, it possesses all the advantages of the latter in this region.

<sup>21a</sup> *Z. physikal. Chem.*, 1914, 87, 1; *A.*, 1914, ii, 430.



In a series of later papers,<sup>22</sup> the range of applicability of the equation has been considered in greater detail. As an equation of condition of considerable accuracy, it appears to be limited to conditions in which the volume is not much less than the critical volume, and it would seem that the influence of temperature on the repulsive forces between the molecules varies from one substance to another. The equation has been criticised by R. Wegscheider<sup>23</sup> on the ground that it entirely fails to accord with the observed compressibility of liquids at low temperatures and high pressures.

The data obtained by Amagat and by Bridgman in their investigations on the compressibility of liquids at high pressures can be satisfactorily represented by a formula<sup>24</sup> based on the differential equation  $\frac{1}{v_0} \left( \frac{dv}{dp} \right)_T = - \frac{a}{K+p}$ , in which the volume change  $dv$  is measured with reference to the volume  $v_0$  (corresponding with  $p = 0$ ),  $a$  is a specific constant, and  $K$ , the internal pressure, is a linear function of  $t = T_c/T$ .

The equation  $(p + a/v^2)(v - b) = RT / \left( 1 + \frac{\psi^2}{T^{1/2}} \right)$ , in which  $\psi$  is a characteristic temperature, is said<sup>25</sup> to accord very well with the behaviour of substances in the gaseous state. At the same time, it yields values for the entropy, internal energy, and heat capacity which are consistent with Nernst's heat theorem.

#### *Vapour Pressures.*

The formulæ commonly employed to express the dependence of the vapour pressure of liquids on the temperature are derived from the Clausius-Clapeyron equation by incorporating the simple gas laws and assuming that the heat of vaporisation can be expressed either as a linear function or as a quadratic function of the temperature. The former assumption leads to the Kirchhoff-Hertz formula, whilst the latter gives the formula usually associated with the name of Nernst. These formulæ involve respectively three and four constants, the values of which may be determined empirically from the observed vapour pressures at three or four different temperatures. For a wider range of temperature, the Nernst formula is in general to be preferred, although in view of the assumed validity of the simple gas laws it may be seriously doubted whether the use of the four-term equation can be justified except for comparatively low vapour pressures.

<sup>22</sup> A. Wohl, *Z. physikal. Chem.*, 1921, **99**, 207, 226, 234; *A.*, ii, 117.

<sup>23</sup> *Ibid.*, 361; *A.*, ii, 192.

<sup>24</sup> H. Carl, *ibid.*, 1922, **101**, 238; *A.*, ii, 477; see also Wohl, *loc. cit.*

<sup>25</sup> W. P. Boynton and A. Bramley, *Physical Rev.*, 1922, **20**, 46.

Simpler formulæ covering a wide range of temperatures have been recently put forward by F. A. Henglein.<sup>26</sup> Denoting by  $T_1$  and  $T_2$  the temperatures at which two different liquids,  $L_1$  and  $L_2$ , have the same vapour pressure, this author has shown that the thermodynamic equation of Clausius-Clapeyron leads to the isobaric temperature formula

$$\log T_1 = a \log T_2 + b \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which  $a$  and  $b$  are constants. Since the coefficient  $a$  is the ratio of the values of  $\lambda/p(v - v')$  for the liquids  $L_2$  and  $L_1$ , it is approximately equal to the ratio of the Trouton numbers, and since the Trouton numbers for normal liquids are nearly identical, it follows from formula (1) that such liquids should obey the simple empirical Ramsay-Young rule,

$$T_1/T_2 = k \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Equation (1) may be written in the form

$$T_1 = C \cdot T_2^a \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $\log C = b$ , and just as the isobaric temperature rule of Ramsay and Young corresponds with the vapour pressure formula

$$\log p = -\frac{k}{T} + C_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which  $C_1$  has the same value for all substances, it is evident that equation (3) corresponds with the vapour pressure formula

$$\log p = -\frac{k}{T^n} + C_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which  $k$  and  $n$  are specific constants and  $C_2$  is a general constant having the same value for all substances.<sup>27</sup> The value of  $n$  is given by  $K \frac{\lambda}{p(v - v')}$ , where  $K$  is independent of the nature of the substance and  $\lambda$ ,  $v$ , and  $v'$  are measured at atmospheric pressure. Having regard to the simple character of this formula, the range of its validity is surprisingly large. It applies equally well to normal and associated liquids, and its general utility has been demonstrated by applying it to sublimation pressures and dissociation pressures. The agreement may be illustrated by a comparison of the observed and calculated vapour pressures of mercury between  $0^\circ$  and  $800^\circ$ .

$T$ (abs.)	$273^\circ$	$383^\circ$	$473^\circ$	$553^\circ$	$633^\circ$	$723^\circ$	$823^\circ$	$1073^\circ$ .
$p$ (obs.)	0.00019	0.013	18.25	158.4	806	4.25	50.0	102.
$p$ (cal.)	0.000198	0.0132	17.6	159.0	811	4.29	49.8	99.5.

<sup>26</sup> *Z. Elektrochem.*, 1920, **26**, 431; *A.*, 1920, ii, 732.

<sup>27</sup> F. A. Henglein, *Z. physikal. Chem.*, 1921, **98**, 1; *A.*, ii, 118.

The pressures up to 633° are recorded in mm.; above this temperature, in atmospheres.

With the object of testing the applicability of the various vapour pressure formulæ, accurate measurements<sup>28</sup> have recently been made of the vapour pressure of lead by determining its boiling point in an atmosphere of nitrogen. The range covered extends from 920° (1.49 mm.) to 1340° (90.3 mm.). Under these low pressures, it may be assumed that the saturated monatomic vapour does not deviate appreciably from the simple gas laws.

It is found that the Nernst formula does not reproduce the experimental results within the limits of the probable errors. When the four constants are calculated from the experimental data for the range 920—1130°, the theoretical curve for the range 1130—1340° falls below the experimental curve to an extent which increases as the temperature rises. On the other hand, if the vapour pressures of lead are compared with those of mercury by making use of the modified isobaric temperature formula of Ramsay-Young, according to which  $T_1$  and  $T_2$  are connected by the formula

$$T_1/T_2 = m + nT_2 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

a very close agreement is observed. In spite of the wide difference between the boiling points, this formula permits of the calculation of isobaric temperatures<sup>29</sup> with an accuracy which lies within the limits of experimental error. Henglein's isobaric temperature formula does not give such good results, although the difference between the observed and calculated values is less than in the case of the Nernst formula. The boiling points of lead ( $p = 760$  mm.) derived by extrapolation from the Ramsay-Young, the Henglein, and the Nernst formulæ are respectively 1619°, 1637°, and 1653°.

According to C. von Rechenberg,<sup>30</sup> it is quite a common occurrence for the vapour pressure curves of different liquids to intersect when the volatilities are of the same order. Such intersection is said to have been established for about two thousand pairs of liquids. It is apparent, however, that with very few exceptions, the intersecting curves are not experimental curves, but have been extrapolated by the application of Dühring's empirical formula on the basis of very meagre experimental data. In these circumstances, it seems quite possible that for a large proportion of the liquid pairs in question, the apparent intersection is a direct consequence of the method adopted in the extrapolation process.

<sup>28</sup> C. K. Ingold, *T.*, 1922, **121**, 2419.

<sup>29</sup> The data for mercury are those recorded by A. Smith and A. C. Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1447.

<sup>30</sup> *Z. physikal. Chem.*, 1921, **99**, 87; *A.*, ii, 120.

For a certain limited number of liquids there is, however, direct experimental proof of the intersection of the respective vapour pressure curves. To pairs of such liquids, the isobaric temperature formulæ of Ramsay-Young and of Henglein would not seem to be applicable. These formulæ take no account of the variation of the heat of vaporisation with the temperature and they can only be expected to apply to pairs of liquids for which the ratio of the heats of vaporisation is independent of the temperature. When one or both of such liquids are polymerised and the degree of polymerisation is a function of the temperature, it may be expected that formulæ of the Kirchhoff-Hertz or Nernst type will more accurately represent the experimental data.

The molecular heats of vaporisation calculated from  $\lambda = 4.23S$ ,<sup>31</sup> where  $S$  is the slope of the approximately straight line curve obtained by plotting  $\log p$  against  $1/T$ , are said to be in better agreement with the experimental values than are the latent heats calculated from the equations of Trouton, Bingham, or Nernst.

The boiling points of liquids which have been exposed to the action of phosphoric oxide for a number of years have been found<sup>32</sup> to be considerably higher than the normal values. The phenomenon is exhibited by liquids of different types, the observed increments ranging from  $14^\circ$  for hexane to  $62^\circ$  for mercury. In support of the view that the change in boiling point is due to polymerisation, preliminary measurements of the temperature coefficient of the surface energy indicate a considerable increment in the association factor. On the other hand, it is rather singular that no measurable differences are shown by the densities of the dried and undried liquids. The non-existence of such differences would seem to emphasise the tentative nature of the polymerisation hypothesis.

### *Crystallisation of Liquids.*

A statistical investigation<sup>33</sup> of the probability of spontaneous crystallisation in supercooled liquids has led to the conclusion that crystallisation is provoked by colloidal dust particles, the effectiveness of which depends on their radius. Immediate crystallisation occurs if the radius of the dust particle is equal to that of a particle of the solid, which, according to thermodynamic considerations, would be in equilibrium with the supercooled liquid. If the dust particles have a smaller radius, the

<sup>31</sup> F. S. Mortimer, *J. Amer. Chem. Soc.*, 1922, **44**, 1429; *A.*, ii, 615.

<sup>32</sup> H. B. Baker, *T.*, 1922, **121**, 568; compare also H. B. Baker and Muriel Baker, *ibid.*, 1912, **101**, 2339.

<sup>33</sup> C. N. Hinshelwood and H. Hartley, *Phil. Mag.*, 1922, [vi], **43**, 78; *A.*, ii, 200.

average life of the supercooled liquid depends on the magnitude of the difference between the actual and the equilibrium radii.

From a study<sup>34</sup> of the number and distribution of the nuclei which are formed when thin films of liquid are allowed to crystallise between glass plates, it has been found that there is a very pronounced tendency for the nuclei to form in the outer zone of the film, particularly at the edge of the cover-glass. It is suggested that this tendency is a surface tension effect.

Experiments<sup>35</sup> made to determine the influence of pressure on the spontaneous crystallisation of supercooled liquids show that pressures up to about a thousand kilograms per square centimetre have very little influence on the number of nuclei which are formed, if the comparison is made at temperatures which are equally removed from the freezing points. The form of the curve which shows the connexion between the number of nuclei and the temperature is not appreciably altered by the application of pressure.

At a fixed temperature, the velocity of crystallisation of supercooled liquids is only slightly affected by subjecting the liquids to high pressures.<sup>36</sup> Since the applied pressure raises the freezing point, it is inferred that the intrinsic effect of the pressure is a diminution in the crystallisation velocity.

There is already a fair amount of evidence favourable to the view that the capacity of substances to form liquid crystals is determined by the molecular configuration, such crystals being formed when the molecules contain a long chain of atoms, and have a definite axis of symmetry. If in benzidine derivatives, which exhibit this property in a marked degree, a  $\text{CH}_2$  group is introduced between the two benzene nuclei, substances are obtained which no longer possess the capacity to form liquid crystals. Similar results are found when the  $\text{CH}_2$  group is replaced by CO, CS, S, or O, but when the interpolated chain is lengthened by the introduction of  $-\text{CH}_2-\text{CH}_2-$  the property reappears. The derivatives of diphenylpropane do not, however, form liquid crystals, but the property reappears again in the derivatives of diphenylbutane. This alternating character is supposed<sup>37</sup> to be connected with the departure of the molecular configuration from the linear chain disposition.

#### *Crystal Structure and the Lattice Elements.*

In a recent lecture<sup>38</sup> to the Chemical Society, Sir W. H. Bragg has discussed the relations between the symmetry of crystals and

<sup>34</sup> K. Schaum, *Z. anorg. Chem.*, 1921, **120**, 241; *A.*, ii, 264.

<sup>35</sup> M. Hasselblatt, *ibid.*, 1921, **119**, 353; *A.*, ii, 35.

<sup>36</sup> *Idem*, *ibid.*, 325; *A.*, ii, 35.

<sup>37</sup> D. Vorländer, *Z. angew. Chem.*, 1922, **35**, 249; *A.*, ii, 554.

<sup>38</sup> *T.*, 1922, **121**, 2766.

the probable symmetry of the molecule. The number of molecules in the unit cell depends on the respective symmetry numbers. If  $N$  is the number of asymmetric molecules which are required to produce crystal symmetry, and  $n$  is the number of molecules in the unit cell, the relation between these numbers is given by  $N = nN'$ , where  $N'$  is the symmetry number of the molecule. Since the great majority of organic crystals are monoclinic prismatic,  $N$  is equal to four and there should be four molecules in the unit cell if the crystal molecule is devoid of symmetry. The unit cells of naphthalene and anthracene contain two molecules, whilst those of acenaphthene,  $\alpha$ - and  $\beta$ -naphthols, benzoic acid,<sup>39</sup> salicylic acid, resorcinol, and 1:2-dinitrobenzene contain four molecules. The numbers of molecules in the unit cell indicated by these considerations are very much smaller than those assigned to the unit by K. Becker and W. Jancke,<sup>40</sup> who have examined a large number of aliphatic and aromatic compounds. Amongst these are included a long series of aliphatic acids, the structure of which varies according to whether the acids contain an even or an odd number of carbon atoms. Acids with an odd number of carbon atoms have a tetragonal lattice with twenty-four or forty-eight molecules in the unit cell. The data for acids with an even number of carbon atoms suggest, on the other hand, either hexagonal symmetry and a unit cell containing seventy-two molecules, or a rhombohedral lattice structure with twenty-four molecules in the unit cell. The alternating structure which is thus indicated by the X-ray examination of the aliphatic acids affords some explanation of the duality which is exhibited by this homologous series in regard to the melting point and other properties.

In these experiments the various substances were examined in the form of compressed pastilles. On submitting these to high pressures, evidence was obtained of a reduction in the volume of the unit cell amounting to about 10 per cent., the changes in the linear dimensions differing considerably according to whether the  $a$ ,  $b$ , or  $c$  dimensions are in question.

An interesting development<sup>41</sup> in the technique of X-ray analysis is afforded by the replacement of homogenous beams by a continuous spectrum of X-radiation. A particular feature of the method is that it permits the use of short-waved penetrating rays and thereby facilitates the investigation of crystals of high absorbing power. Furthermore, the measured distances between the

<sup>39</sup> Sir W. H. Bragg, *Proc. Physical Soc.*, 1921, **34**, 33; *A.*, ii, 28.

<sup>40</sup> *Z. physikal. Chem.*, 1921, **99**, 242, 267; *A.*, ii, 128.

<sup>41</sup> G. L. Clark and W. Duane, *Proc. Nat. Acad. Sci.*, 1922, **8**, 90; *A.*, ii, 483.

planes of atoms are independent of the constants of any other crystal.

The fact that the intensity of reflected X-radiation falls off rapidly as the glancing angle is increased has been interpreted <sup>42</sup> as evidence that the scattering power is not a localised effect but is the result of reflections originating in centres distributed throughout the atomic volume. From the form of the scattering curves, attempts have been made to determine the distribution of the electrons round the atomic nuclei.

From the behaviour of lithium fluoride, P. Debye and P. Scherrer came to the conclusion <sup>43</sup> that the relative numbers of the electrons surrounding the nuclei of fluorine and lithium are in the ratio 10:2. This would suggest that the valency electron of lithium (atomic number 3) has been transferred to the fluorine atom (atomic number 9) and might be interpreted as evidence favourable to the view that the constituents of such polar compounds are ionic and that the mechanism involved in the combination of polar elements is of the type postulated in the Lewis-Langmuir theory. The above value of the electron ratio depends, however, on an extrapolation of the actually measured scatterings to zero glancing angle, and for this and other reasons it would seem necessary to accept the conclusion with some reserve.

More recent observations <sup>44</sup> on crystals of sodium chloride, in which an attempt has been made to determine the absolute values of the scattering power of the sodium and chlorine atoms, represent a definite advance in the attack on the problem of electron distribution. From the data for the scattering at a series of glancing angles, curves are drawn which show the electron density at gradually increasing distances from the atomic centres. Hypothetical models of various kinds may obviously be tested by reference to these curves, which would appear to be definitely inconsistent with certain configurations which have been suggested for the sodium and chlorine atoms. Such excluded models of sodium chloride are those in which the sodium and chlorine atoms are represented as having outer shells containing eight electrons. An electron distribution of this type is inadmissible, whether the electrons be supposed to revolve in circular orbits of the same radius or to revolve in orbits on the same sphere. The experiments do not, as yet, indicate whether the valency electron of

<sup>42</sup> Sir W. H. Bragg, *Phil. Trans.*, 1915, [A], 215, 253; A. K. Compton, *Physical Rev.*, 1917, 9.

<sup>43</sup> *Physikal. Z.*, 1918, 19, 474; *A.*, 1919, ii, 20.

<sup>44</sup> W. L. Bragg, R. W. James, and C. K. Bosanquet, *Phil. Mag.*, 1922, [vi], 44, 433; *A.*, ii, 703.

sodium has been transferred to the chlorine. The difficulty in reaching a decision on this point is at once evident, when consideration is given to the fact that the distance between the centres of sodium and chlorine atoms is 2.81 Å., whilst the electron distribution curve (based on the measurement of the scattering power) extends to 1.0 Å. from the centre of the sodium atom and to 1.8 Å. from the centre of the chlorine atom.

### *Ionisation of Electrolytes.*

The reception accorded to the views of Ghosh on the nature of solutions of electrolytes by the authors of certain well-known text books would seem to imply that these views have acquired the status of a well-established theory. The critical discussion of the theory by J. R. Partington,<sup>45</sup> D. L. Chapman and H. J. George,<sup>46</sup> H. Kallman,<sup>47</sup> C. A. Kraus,<sup>48</sup> J. Kendall,<sup>49</sup> and S. Arrhenius<sup>50</sup> conveys an entirely different impression and it is obvious that the Ghosh hypothesis is in many ways far from satisfactory as a basis for the interpretation of the behaviour of electrolytes. In particular, the facts and arguments adduced by Kendall represent a very strong case against the theory. The fundamental postulates are claimed to be inconsistent with one another, and by reason of the fact that an incorrect value has been assigned to the electrical work which is necessary to separate and disperse the ions from the average positions which they are supposed to take up in the postulated space lattice, all the equations derived by Ghosh are erroneous. Contrary to the requirements of the Ghosh theory, electrolytes of the same type are not equally ionised at equivalent concentrations, and the variation of  $\mu/\mu_\infty$  with temperature cannot be explained in terms of the change in the dielectric constant of the solvent medium. In the case of electrolytes of the simplest type, the osmotic coefficients derived from freezing-point data agree better with the values given by  $i = 1 + \alpha$  (Arrhenius) than with those given by the Ghosh formula, according to which  $i = 2 \left( 1 - \frac{1}{3} \log \frac{1}{\alpha} \right)$ . Furthermore, in solvents of low dielectric capacity, the proportion of free ions should increase very rapidly with the dilution; the observed rate of increase is much smaller than that predicted by the theory.

This brief summary is sufficient to give some idea of the failure

<sup>45</sup> *Trans. Faraday Soc.*, 1919, 15, 98; *A.*, 1920, ii, 151.

<sup>46</sup> *Phil. Mag.*, 1921, [vi], 41, 799; *A.*, ii, 371.

<sup>47</sup> *Z. physikal. Chem.*, 1921, 98, 433; *A.*, ii, 125.

<sup>48</sup> *J. Amer. Chem. Soc.*, 1921, 43, 2514; *A.*, ii, 256.

<sup>49</sup> *Ibid.*, 1922, 44, 717; *A.*, ii, 419.

<sup>50</sup> *Z. physikal. Chem.*, 1922, 100, 9; *A.*, ii, 345.



of the Ghosh theory. The whole of the postulates involved in the theory are not thereby invalidated. There is, indeed, a growing tendency to regard more favourably the view that the strongly polar compounds are completely ionised and that the ratio  $\mu/\mu_\infty$  has not the significance attached to it in the theory of Arrhenius.

The refractive powers of electrolytes considered in the light of the dispersion theory have led to the conclusion<sup>51</sup> that there are considerable differences between the refractivities of atoms and the corresponding ions. A comparison of the refractivities of weak and strong electrolytes in aqueous solution indicates that the molecules of such substances can exist in two forms, one of which contains uncharged atoms or groups, whilst in the other "polarised" form, the constituent atoms or groups carry electric charges. Free ions and the ions in polarised molecules have the same structure and the same optical properties, which differ from those of the corresponding atoms or groups in the non-polarised molecules.

An attempt has been made<sup>52</sup> to determine the degree of ionisation of fused salts by measuring the refractivities.

The ionisation of picric acid,<sup>53</sup> dissolved in acetone, conforms to the requirements of the dilution law, the ionisation constant being of the order  $1 \times 10^{-6}$ . In aqueous acetone containing 6.2 per cent. of water, the dilution law is no longer satisfied. When the dilution is increased from 32 to 1024 litres, the value of  $\alpha^2/(1 - \alpha)v$  decreases some 50 per cent., which is approximately the deviation observed when the picric acid is dissolved in pure water. Since the "constant" for the aqueous acetone solutions is only about one-hundredth of the "constant" given by pure aqueous solutions, it would appear that the anomalous behaviour of strong electrolytes cannot be attributed to the high value of the degree of ionisation.

#### *Electrical Conductance.*

The experimental study of the mechanism of electrical conduction in solid binary compounds has not, until recently, given very clearly defined results. The difficulties incidental to transport measurements in solid conductors have, however, been overcome by C. Tubandt, who by this means has obtained positive information relative to the nature of the conducting process. The silver halides, lead chloride, and lead fluoride are electrolytic conductors. In the case of the silver compounds, the current is

<sup>51</sup> J. A. Wasastjerna, *Z. physikal. Chem.*, 1922, 101, 193; *A.*, ii, 491

<sup>52</sup> G. Meyer and A. Heck, *Z. Elektrochem.*, 1922, 28, 2; *A.*, ii, 241; *Z. physikal. Chem.*, 1922, 100, 316; *A.*, ii, 329.

<sup>53</sup> S. M. Neale, *Trans. Faraday Soc.*, 1922, 17, 505; *A.*, ii, 420.

carried exclusively by the positive ions, whereas the carriers in the lead compounds are the negative ions.<sup>54</sup> Cuprous sulphide, in the form which is stable above 91°, and silver sulphide in the form stable above 180° behave exactly like the silver halides. The  $\beta$ -form of silver sulphide, stable below 180°, is, however, a mixed conductor,<sup>55</sup> about 80 per cent. of the conduction being electrolytic and the remaining 20 per cent. metallic. As in the case of the  $\alpha$ -form, the electrolytic conduction is due entirely to the movement of the silver ions. The passage of a current through  $\beta$ -silver sulphide is consequently a process in which positive electricity is conveyed by charged atoms, whilst negative electricity is conveyed in the opposite direction in the form of free electrons. The mechanism is therefore the same as that suggested by Kraus for the conductance of solutions of the alkali metals in liquid ammonia. The conductivity of these solutions increases rapidly<sup>56</sup> with increasing concentration, such that in saturated solutions at the boiling point of liquid ammonia, the atomic conductance of the alkali metals is considerably greater than the atomic conductance of mercury.

Interesting results have also been obtained<sup>57</sup> in the investigation of the mode of conduction of the current through mixtures of silver sulphide and metallic silver.

In measuring conductivities of solutions, the telephone receiver can be conveniently replaced<sup>58</sup> by a galvanometer in combination with a thermionic valve. A new differential method<sup>59</sup> is said to have given good results.

### *Potential Differences.*

Low-voltage standard cells are described<sup>60</sup>; the combination Cd amalgam|CdI<sub>2</sub>|PbI<sub>2</sub>|Pb amalgam gives a constant and readily reproducible  $E.M.F. = 0.09838$  volt at 20°.

Measurements<sup>61</sup> of the electrode potential H<sub>2</sub>|HCl + KCl are said to afford evidence of the hydration of the hydrogen-ions.

The study<sup>62</sup> of electrodes of the type illustrated by the two examples,

<sup>54</sup> C. Tubandt and S. Eggert, *Z. anorg. Chem.*, 1920, **110**, 196; *A.*, 1920, ii, 279. C. Tubandt, *ibid.*, 1921, **115**, 105; *A.*, 1921, ii, 426.

<sup>55</sup> C. Tubandt, S. Eggert, and G. Schibbe, *ibid.*, 1921, **117**, 1; *A.*, 1921, ii, 480.

<sup>56</sup> C. A. Kraus and W. W. Lucasse, *J. Amer. Chem. Soc.*, 1922, **43**, 2529; *A.*, ii, 252.

<sup>57</sup> C. Tubandt and S. Eggert, *Z. anorg. Chem.*, 1921, **117**, 48; *A.*, 1921, ii, 480.

<sup>58</sup> M. Abribat, *Bull. Soc. chim.*, 1922, [iv], **31**, 241; *A.*, ii, 344.

<sup>59</sup> L. Rolla and L. Mazza, *Gazzetta*, 1922, **52**, i, 421; *A.*, ii, 544.

<sup>60</sup> J. Oblata, *Proc. Phys. Math. Soc. Japan*, 1921, [vii], **3**, 136; *A.*, ii, 343.

<sup>61</sup> E. Schreiner, *Z. anorg. Chem.*, 1922, **121**, 321; *A.*, ii, 468.

<sup>62</sup> G. Trümpler, *Z. physikal. Chem.*, 1921, **99**, 9; *A.*, ii, 110.

Ag|AgBr|KBr solution saturated with bromine  
and Cu|CuS|Na<sub>2</sub>S solution saturated with sulphur,

indicates that there is an essential difference between such electrodes according to whether the solid binary compound is an electrolytic conductor (AgBr) or a metallic conductor (CuS). The experimental data suggest a fundamental difference in the structure of the two classes of compounds and the conclusion is drawn that the lattice elements of the compounds of the former group are ions, whilst those of the compounds which show metallic conduction consist of uncharged atoms.

### *Velocity of Hydrolytic Reactions.*

A considerable amount of attention has been directed to the further investigation of the hydrolysis of sucrose and the esters. Although these reactions can be satisfactorily represented in terms of the ordinary velocity coefficient when the concentrations of the hydrolyte and the catalysing acid are fixed, it is well known that variations in the concentrations of the reactants produce changes in the velocity coefficient which suggest that the active masses of the hydrolyte, water, and catalyst are not appropriately measured by the respective volume concentrations. In recent work, the attempt has been made to replace volume concentrations by the activities or thermodynamic concentrations, the value of which, as shown by G. N. Lewis and M. Randall,<sup>63</sup> may be determined in a consistent manner from vapour pressure or osmotic data, and in the case of ionic reactants from potential difference measurements. To what extent the thermodynamic concentrations may afford a measure of the active mass of chemical reactants is a matter which can only be decided by experiment, and at the present time there appears to be no adequate ground for the presumption that thermodynamic concentrations provide a clue to the apparent deviations from the law of mass action.

Some experiments<sup>64</sup> on the rate of inversion of sucrose are interpreted in favour of the view that the hydrogen-ion and the un-ionised acid are both catalytically active. Other measurements<sup>65</sup> are said to be in agreement with the equation  $dx/dt = ka_w^6 \cdot a_H \cdot (c_s - x)$ , in which  $a_w$  and  $a_H$  are the activities of the water and the hydrogen-ion. According to this equation, the reaction is of the sixth order in so far as the water is concerned.

<sup>63</sup> *J. Amer. Chem. Soc.*, 1921, 43, 233; *A.*, 1921, ii, 241; *ibid.*, 1150; *A.*, 1921, ii, 427.

<sup>64</sup> R. H. Clarke, *ibid.*, 1759; *A.*, ii, 135.

<sup>65</sup> G. Scatchard, *ibid.*, 2387; *A.*, i, 230.

Experiments with sucrose <sup>66</sup> and ethyl acetate <sup>67</sup> in which the concentration of the hydrolyte was kept constant and the concentration of the catalysing acid was varied between wide limits lead to the conclusion that the reaction velocity is not by any means accurately proportional to the activity of the hydrogen-ion. The inversion data obtained with hydrochloric acid and acetic acid would indeed suggest that the specific character of the acid cannot be ignored.

Other observations <sup>68</sup> on the velocity of inversion, in which the concentration of the sucrose was varied from 100 to 700 grams per litre, have been found to yield a constant velocity coefficient when the participation of the sucrose, water, and hydrogen-ion is supposed to be proportional to the activities. The derivation of this coefficient involves, however, a number of other assumptions, namely, that the sucrose is mainly present in the solution in the form of a tetrahydrate, that the rate of inversion is determined by the rate of combination of a hypothetical sucrose dihydrate with the hydrogen-ion, and that the activity of the latter is very largely influenced by the viscosity of the medium. In these circumstances, it is very difficult to say whether the measurements in question are to be regarded as favourable or otherwise to the view that the active masses of the reactants are to be expressed in terms of the thermodynamic concentrations.

Measurements <sup>69</sup> of the rate of hydrolysis of ethyl acetate in presence of strong acids and varying quantities of the corresponding salts are said to indicate that the velocity is proportional to the cube root of the activity of the hydrogen-ion.

The initial velocities with which methyl and ethyl acetate are hydrolysed have been measured <sup>70</sup> at higher temperatures in presence of regulator mixtures, for each of which the  $p_H$  value was electrometrically determined. The velocity of hydrolysis shows a minimum at a definite hydrogen-ion concentration, but the curve obtained by plotting the velocity as a function of  $p_H$  is by no means symmetrical about the minimum point. The curve rises more steeply on the alkaline side of the "critical"  $p_H$  value, and from this, it may be inferred that the assumptions made by Wijs <sup>71</sup> in his determination of the degree of ionisation of water, are

<sup>66</sup> H. A. Fales and J. C. Morrell, *J. Amer. Chem. Soc.*, 1922, 44, 2071; *A.*, ii, 832.

<sup>67</sup> H. S. Harned and R. Pfanstiel, *ibid.*, 2193; *A.*, ii, 832.

<sup>68</sup> T. Moran and W. C. McC. Lewis, *T.*, 1922, 121, 1613.

<sup>69</sup> G. Åkerlöf, *Z. physikal. Chem.*, 1921, 98, 250; *A.*, ii, 134.

<sup>70</sup> K. G. Karlsson, *Z. anorg. Chem.*, 1921, 119, 69; *A.*, ii, 40.

<sup>71</sup> Compare *A.*, 1893, ii, 364; 1894, ii, 82.

unjustified. The presence of neutral salts does not affect the  $p_H$  value, for which the initial velocity of hydrolysis is a minimum.

Measurements <sup>72</sup> of the velocity of saponification of esters by potassium hydroxide in mixtures of ethyl alcohol and water show that the velocity coefficient is not a continuous function of the composition of the solvent. When the coefficients, measured at 15°, are plotted against the composition, a graph is obtained which consists of a series of straight lines intersecting at points which correspond closely with alcohol-water mixtures in which the components are present in simple molecular ratios. This coincidence is regarded as an indication of the formation of stable alcohol-water complexes. For the most part, the results appear to be independent of the nature of the ester. Furthermore, at higher temperatures, the number of discontinuities observed is smaller, indicating that the less stable complexes have disappeared. The interpretation given to the experimental data is said to be supported by the evidence afforded by the curves representing the variation of the physical properties of alcohol-water mixtures with the composition. Such curves are, however, for the most part, continuous and their interpretation is a matter of great difficulty. The difference between these curves and the discontinuous velocity curves is striking, but it seems possible that it may be due to the much greater susceptibility of reaction velocity to slight changes in the character of the solvent medium. On the other hand, it is rather remarkable that other reactions which have been studied in aqueous alcoholic media show no evidence of the discontinuities disclosed by the ester hydrolysis curves.

### *Combustion of Gases.*

Considerations based on measurements of the speed of the uniform movement of flame in complex mixtures, that is to say, mixtures which contain oxygen and two or more combustible gases, have suggested <sup>73</sup> a new basis for the interpretation of the partition of the oxygen between the several combustible gases when the supply of oxygen is insufficient for complete combustion.

Under identical conditions, the speeds of propagation of flame are the same for all limit mixtures, provided that these are of the same type, that is, upper or lower limit mixtures. If the limit mixture of air and a combustible gas, A, is mixed with the limit mixture of air and a second combustible gas, B, the speed of propagation of flame in the resultant complex mixture is the same

<sup>72</sup> H. McCombie, H. A. Scarborough, and R. H. Settle, *T.*, 1921, 119, 970; 1922, 121, 243, 2308.

<sup>73</sup> W. Payman and R. V. Wheeler, *ibid.*, 1922, 121, 363.

as the speed characterising the simpler limit mixtures, and this equality holds no matter what may be the proportion in which the simple limit mixtures are present in the complex mixtures.

Other observations lead to the conclusion that this "law of speeds" is not a particular relation applicable only to limit mixtures, but that it holds for all complex mixtures, provided that the corresponding simple mixtures are of the same type.

So far as the propagation of flame is concerned, it follows that the air in the complex mixture,  $A + B + \text{air}$ , may be considered to be divided between A and B in such a way that the speeds of propagation of flame in the hypothetical simple mixtures,  $A + \text{air}$  and  $B + \text{air}$ , would be the same as it actually is in the complex mixture.

The products resulting from the passage of flame through a mixture of methane, hydrogen, and oxygen, in which the oxygen present is insufficient for the complete combustion of both combustible gases, should therefore be the same as would be obtained if the methane were mixed with a certain proportion of the oxygen, and the hydrogen with the remainder, and the two simple mixtures were separately exploded. Observations indicate in fact that this identity is actually obtained when the oxygen is distributed between the methane and the hydrogen so as to produce simple inflammable mixtures which are characterised by the same velocity of propagation of flame.

It has been supposed,<sup>74</sup> although the view has by no means been generally accepted, that the relative quantities of the two sets of products formed in the explosion of mixtures of two combustible gases with insufficient oxygen, afford a measure of the "relative affinities" of the two gases for oxygen. The considerations advanced by Payman and Wheeler indicate that the relative quantities of the products cannot be regarded as an effect of "affinity," but are a direct consequence of the fact that a methane-oxygen mixture, which has the same speed of flame as a given hydrogen-oxygen mixture, contains a considerably larger proportion of oxygen.

Further evidence<sup>75</sup> has been obtained in support of Le Chatelier's rule that when two or more limit mixtures containing different combustible gases are mixed, the resulting complex mixture is also a limit mixture. It appears, however, that there are exceptions to the rule and considerable deviations are found<sup>76</sup> when one of the combustible gases concerned is capable of propagating a cool flame. The propagation of this appears to be hampered

<sup>74</sup> W. A. Bone, *Phil. Trans.*, 1915, [A], 215, 275.

<sup>75</sup> R. G. Boussu, *Compt. rend.*, 1922, 175, 30; *A.*, ii, 557.

<sup>76</sup> A. G. White, *T.*, 1922, 121, 2561.

by the presence of the second combustible gas, the resulting disturbance varying considerably with the nature of the latter.

*The Radiation Theory of Chemical Change.*

According to the simple form of the radiation theory,<sup>77</sup> the frequency of the radiation which transforms the molecules of a substance into a reactive condition can be calculated from the temperature coefficient of the velocity of the reaction. It is assumed that each molecule absorbs one quantum of the radiant energy in question. One of the objections raised against this view of the reaction mechanism is that the reacting substance shows no absorption band in the region of the calculated wave-length. The supporters of the theory contend, however, that such, apparently simple, reactions may involve a series of consecutive changes, which, although they cannot be differentiated by any known experimental method, are sharply separated and clearly defined in terms of the associated energy quanta. In such a reaction, the energy absorbed per molecule will be represented as the sum of a number of smaller quanta which may, according to certain lines of evidence, bear some simple relation to one another.<sup>78</sup> In these circumstances, the bands in the absorption spectrum of the reacting substance will correspond with wave-lengths greater than that which is indicated by the simple radiation hypothesis. Infra-red bands corresponding with simple multiples of the calculated wave-length have in fact been found in the spectrum of nitrogen pentoxide, although no absorption occurs in the spectral region indicated by the simple theory. The radiation theory has also been criticised on the ground that the rate of supply of energy of the requisite frequency is totally inadequate to account for the observed rate of the chemical change. The validity of the argument is questionable. In any case, J. Perrin<sup>79</sup> points out that if the energy of activation corresponds with the absorption of a number of relatively small quanta, the requisite amount of energy is available in quantities more than sufficient to account for the observed velocity. On the other hand, W. C. McC. Lewis<sup>80</sup> contends that this objection falls to the ground, because it ignores the redistribution of the radiant energy which immediately ensues when radiation of a particular wave-length is removed.

A third criticism to which the radiation theory has been sub-

<sup>77</sup> Papers contributed to a general discussion arranged by the Faraday Society give a clear indication of the present position of the radiation theory; see *Trans. Faraday Soc.*, 1922, 17, Part I; *A.*, ii, 628.

<sup>78</sup> E. C. C. Baly, *loc. cit.*, p. 588.

<sup>79</sup> *Loc. cit.*, p. 546.

<sup>80</sup> *Loc. cit.*, p. 573.

jected is that the reaction velocities are apparently unaffected by the directed radiation from external sources, although in such circumstances the density of the supposedly active radiation is enormously increased. This objection is also countered by the supposition that the energy of activation is the sum of a series of smaller quanta, and there would seem to be no necessity for Lewis's view that the effect of the active radiation is nullified by absorption in the solvent medium. The fact that the rate of inversion of sucrose by hydrochloric acid is not measurably altered<sup>81</sup> when the solution, in the form of a cloud of fine droplets, is subjected to the action of a beam of bright sunlight would seem to show that the latter view is untenable.

Summarising the position, it would appear that the radiation hypothesis cannot be reconciled with the facts so long as the energy of activation,  $E$ , is represented by the equation  $E = Nh\nu$ , where  $N$  is the Avogadro number,  $h$  the Planck quantum constant, and  $\nu$  the frequency of the activating radiation. The simplicity of the relations involved in this equation constitutes probably the most attractive feature of the radiation hypothesis and if, as would seem to be the case, it is necessary to replace the above equation by one of the form  $E = Nh(n_1\nu_1 + n_2\nu_2 + n_3\nu_3 \dots)$ , in which  $n_1, n_2, n_3 \dots$  are small integral numbers, then we have to deal with a modified radiation theory which, generally speaking, is no longer amenable to the test of experiment until such time as infra-red absorption spectra have been studied in a very thorough and comprehensive way.

There is always the possibility that in certain cases the general equation may be reduced to its simplest form. An example is said to be furnished by the decomposition of triethylsulphonium bromide,<sup>82</sup> the absorption spectrum of which has been examined in a number of solvents, in which the rate of decomposition had been previously measured at different temperatures by von Halban.<sup>83</sup> In the six solvents, where the reaction follows a normal course, maximum absorption is found to occur at a radiation frequency which agrees closely with that calculated from the temperature coefficient of the reaction velocity.

The two important facts which may be considered mainly responsible for the attention which has been given to the radiation hypothesis are that the hypothesis affords a plausible explanation of the effect of temperature on reaction velocity and provides a

<sup>81</sup> T. W. J. Taylor, *Nature*, 1921, 103, 210; *A.*, ii, 336; compare also W. C. McC. Lewis, *ibid.*, 241; *A.*, ii, 336.

<sup>82</sup> W. C. McC. Lewis, *T.*, 1922, 121, 665.

<sup>83</sup> *Z. physikal. Chem.*, 1909, 67, 129.



basis for the interpretation of the mechanism of unimolecular reactions. It has, however, been pointed out,<sup>84</sup> that if the energy of activation corresponds with an additive series of quanta, the observed dependence of reaction velocity on the temperature is not that which would be indicated by the radiation theory. On the other hand, it may be doubted<sup>85</sup> whether there is any known instance of a chemical change in which the molecules of a substance are transformed independently of one another and of foreign molecules. A critical examination of the facts suggests rather that in all such chemical changes there is interaction between two or more molecules. Radioactive disintegration processes are not exceptional, for in such changes the chemical valency electrons are not involved, and, moreover, there is no temperature coefficient to be accounted for.

J. Plotnikow<sup>86</sup> criticises the law of photochemical equivalence on the ground that it is incompatible with the Grotthus-van't Hoff law, and that it leads to an impossible value for the chemical activity of radiant energy, the frequency of which is of the same order as that of Röntgen rays.

The thermal decomposition of formic acid<sup>87</sup> gives rise to two sets of products, namely, (a) carbon dioxide and hydrogen, (b) carbon monoxide and water. At 283°, the two reactions take place with the same velocity. From a consideration of the respective energies of activation it would appear that the formic acid should be exclusively decomposed into carbon monoxide and water. If the facts are to be interpreted in accordance with the simple radiation theory, it is necessary to introduce qualifying assumptions and the suggestion is made that the second reaction occurs on the walls of the containing vessel and that its velocity is enormously reduced by the surface conditions.

According to Perrin, fluorescence consists in the emission of characteristic radiation by the molecules of certain substances which are decomposed by light. This view is not in agreement with experiments which have been made by R. W. Wood.<sup>88</sup> For instance, it has been found that an aqueous solution of rhodamine is almost non-fluorescent at 100°, although at this temperature it is decomposed by light as rapidly as it is at the ordinary temperature. Perrin's theory further takes no account of the part played by oxygen in the photochemical decomposition of fluores-

<sup>84</sup> F. A. Lindemann, *Trans. Faraday Soc.*, 1922, 17, 598.

<sup>85</sup> See, for instance, T. M. Lowry, *ibid.*, p. 596.

<sup>86</sup> *Z. wiss. Photochem.*, 1922, 21, 134; *A.*, ii, 248.

<sup>87</sup> C. N. Hinshelwood, H. Hartley, and B. Topley, *Proc. Roy. Soc.*, 1922, [A], 100, 575; *A.*, ii, 274.

<sup>88</sup> *Phil. Mag.*, 1922, [vi], 43, 757; *A.*, ii, 334.

cent substances. The intensity of the fluorescence exhibited by a hydrochloric acid solution of fluorescein is independent<sup>89</sup> of the amount of oxygen present, although the rate of decomposition varies over a considerable range inversely as the oxygen content of the solution. In oxygen-free solutions, fluorescein is moreover stable towards light.

An interesting contribution<sup>90</sup> has been made to the photochemistry of silver compounds. It is shown that silver chloride is itself non-sensitive to light, and that the active absorbent of the light energy is the colloidal metallic silver which is present in very small amounts in fresh unilluminated silver chloride emulsions.

### *Disperse Systems and Colloidal Solutions.*

Elutriation experiments,<sup>91</sup> made with powdered barytes and quartz, show that the rate of fall of small particles through water is not in agreement with the "law of viscous resistance," which states that the velocity varies as the square of the diameter. On the contrary, the connexion between the diameter,  $d$ , and the velocity,  $v$ , for particles of a given substance falling through water at a fixed temperature is given by the formula  $\log d = \log a + kv$ , in which  $a$  and  $k$  are constants. Under identical conditions, the sectional areas of the barytes and quartz particles which fall with the same velocity are in the same ratio as the gravitational forces which act on the two kinds of particles.

When Stokes's law is applied to the determination of the radius of the particles immersed in a liquid, no account is usually taken of the effect produced by adsorption. If  $r_0$  denote the radius calculated in this way,  $r$  the true radius, and  $a$  the quantity of liquid adsorbed by one gram of the solid, then the relation<sup>92</sup> between these quantities is given by  $r^2 = r_0^2 \left(1 + a \frac{v_l}{v_s}\right)$ , where  $v_l$  and  $v_s$  are the specific volumes of the liquid and solid respectively. On the assumption that the obvious external surface is responsible for the adsorption, this equation may be employed to determine an upper limit for the thickness of the adsorption layer.

The law of distribution of colloidal particles which represents the experimental data obtained by Perrin for suspensions of gamboge in water would appear to be limited in its application to a very narrow region below the surface of the suspensoid system. Observ-

<sup>89</sup> F. Weigert, *Z. Physik*, 1922, **10**, 349; *A.*, ii, 681.

<sup>90</sup> F. Weigert and W. Schöller, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 641; *A.*, ii, 10.

<sup>91</sup> T. M. Lowry and L. P. McHatton, *Trans. Faraday Soc.*, 1922, **18**, 19.

<sup>92</sup> A. M. Williams, *ibid.*, p. 53.

ations<sup>93</sup> on colloidal solutions of copper have shown that the particles are uniformly distributed, samples taken from a column, 90 cm. in height, which had been left undisturbed for fifty days, showing no measurable difference in concentration.

A further investigation<sup>94</sup> of gamboge suspensions, in which the counting of the particles at different depths was effected by a modified arrangement of the Zeiss ultra-microscope, shows that there are apparently three well-defined regions in a suspensoid system in addition to the surface layer, the thickness of which is only of the order of the range of intermolecular forces. The first of the three is the Perrin region, less than 0.1 mm. in thickness, in which the distribution of the particles is analogous to the distribution of the molecules in a column of gas; the second is a region, the thickness of which appears to be of the order of 1 mm., in which the departure from the logarithmic distribution formula becomes more and more pronounced as the distance from the surface increases; the third region is represented by the bulk of the suspension in which the distribution of the particles is sensibly uniform. The actual average results of the counts made in these experiments are shown in the accompanying table, in which  $y$  denotes the depth of the layer examined below the surface and  $n$  represents the number of particles per unit of volume:

$y$ (cm.) .....	0.023	0.033	0.043	0.063	0.083	0.103	0.123	0.143
$n \times 10^6$ .....	0.95	2.14	3.61	7.14	8.69	9.53	9.76	9.76

These numbers refer for the most part to the layer between the Perrin layer and the bulk of the suspension. Theoretical considerations put forward independently by Burton and by Porter lead to equations which are in agreement with the observed distribution in this transition layer.

If a measured volume of the saturated solution of a lead salt containing one of its radioactive isotopes is shaken up with a weighed quantity of the finely-powdered solid (free from the isotope), it may be assumed that the isotope will distribute itself between the surface of the solid and the solution in the same ratio as the lead. By measuring the change in the radioactivity of the solution, it is possible to estimate<sup>95</sup> the surface area of the finely divided solid lead salt. A convenient summary of other applications of radioactive substances in the investigation of molecular dynamics is given in a paper under the title "Radioactive Indicators."<sup>96</sup>

<sup>93</sup> E. F. Burton and (Miss) E. Bishop, *Proc. Roy. Soc.*, 1921, [A], **100**, 414.

<sup>94</sup> A. W. Porter, *Trans. Faraday Soc.*, 1922, **18**, 91.

<sup>95</sup> F. Paneth and W. Vorwerk, *Z. physikal. Chem.*, 1922, **101**, 445; *A.*, ii, 618.

<sup>96</sup> F. Paneth, *Z. angew. Chem.*, 1922, **35**, 549; *A.*, ii, 785.

Facts are adduced<sup>97</sup> in support of the view that, in certain cases at least, the adsorption of radioactive substances from solution is not primarily determined by the colloidal condition of the adsorbent but by its chemical nature.

Liquids which have been adsorbed by porous substances appear to be subjected to a very high degree of compression as a result of the action of molecular forces.<sup>98</sup> The change in the volume of water adsorbed in the micro-pores of charcoal is probably of the order of 25 per cent. and in the case of ether about 40 per cent.

The conditions determining the formation of amorphous or crystalline solids in precipitation changes are discussed by F. Haber.<sup>99</sup> It is to be expected that the rate at which the primary non-orientated aggregates will be transformed into ordered lattice formations will be greatest in the case of binary compounds, in which the polarity is most marked. When the polarity is less strongly accentuated, the compounds will tend to remain in the primary form of amorphous precipitate or sol.

Zeolites, when partly or completely dehydrated, absorb gases in large quantities.<sup>1</sup> In general, the volumes of the different gases which are taken up, increase in the order of the respective critical temperatures. Hydrogen is, however, absorbed in exceptionally large quantities, and the behaviour of hydrogen and certain other gases suggests that these enter into the crystal lattice in the position previously occupied by the water of hydration.

The connexion between the coagulating power of ions and the concentration of the disperse phase is found<sup>2</sup> to depend on the nature of the latter. For colloidal solutions of chromic oxide, Prussian blue, and ferric oxide, the coagulating ion-concentration decreases as the concentration of the colloid decreases, irrespective of the valency of the ion. On the other hand, when the disperse-phase is arsenious sulphide, the relation between the concentrations of the ion and of the colloid varies very considerably according to the valency of the ion. The differences in behaviour are attributed to the relative adsorbabilities of the coagulating positive ion and of the stabilising negative ion.

The action of protective colloids<sup>3</sup> in retarding changes of state is shown very clearly in the precipitation of mercuric iodide in

<sup>97</sup> E. Ebler and A. J. van Rhyn, *Ber.*, 1921, **54**, [B], 2896; *A.*, ii, 16.

<sup>98</sup> W. D. Harkins and D. T. Ewing, *J. Amer. Chem. Soc.*, 1921, **43**, 1787; *A.*, ii, 123.

<sup>99</sup> *Ber.*, 1922, **55**, [B], 1717; *A.*, ii, 553.

<sup>1</sup> R. Feiliger and K. Lapkamp, *Physikal. Z.*, 1921, **22**, 563; *A.*, ii, 30.

<sup>2</sup> H. B. Weiser and H. O. Nicholas, *J. Physical Chem.*, 1921, **25**, 742; *A.*, ii, 266; E. F. Burton and E. D. MacInnes, *ibid.*, 517; *A.*, ii, 130.

<sup>3</sup> J. N. Friend, *Nature*, 1922, **109**, 341; *A.*, ii, 267.

presence of one per cent. of gelatin. The initially precipitated yellow modification remains unchanged for a considerable time.

The conclusions which have been drawn from the study of soap solutions by the application of various osmotic methods and by measurements of conductivity, potential differences, and catalytic activity have been confirmed in a remarkable way <sup>4</sup> by the behaviour of the solutions when they are subjected to ultra-filtration. Not only has an independent check on the results of previous work been thereby obtained, but it is shown that ultra-filtration affords a method for the separation of the ionic micelle from the neutral colloid, for the determination of the degree of hydration of the colloidal constituents, and for the approximate determination of the dimensions of the charged and uncharged colloidal particles. The ionic micelle is mainly composed of aggregated ions with water of hydration, whilst most of the neutral colloid is present in quite separate particles of much larger dimensions.

The theory of ultra-filtration is discussed and on the assumption that pores of a given diameter will allow particles of a smaller diameter to pass through provided that the applied pressure is greater than the osmotic pressure of the constituents which are coarse enough to be held back by the pores, it is found that the experimental results can be adequately explained.

The ultra-filtration method has already been applied in the investigation of other colloid-electrolyte systems. The successful application of the method would seem to depend on the rapidity with which any disturbance of the internal equilibrium is annulled in comparison with the speed of the ultra-filtration process.

The properties of hexadecanesulphonic acid <sup>5</sup> indicate that this acid is a typical colloidal electrolyte having all the characteristic properties of the alkali-metal soaps. Ring compounds are far less colloidal than the corresponding open-chain compounds, indicating that the linear extension of the molecule is an important factor in producing a colloidal electrolyte.

Soap solutions, to which the corresponding alkali metal chloride has been added in quantities insufficient to cause salting out, are found <sup>6</sup> to contain the soap for the most part in the form of neutral colloid, the proportion of ionic micelle being much smaller than in pure soap solutions.

The consideration of the salting-out process from the point of view of phase equilibrium leads to the conclusion <sup>7</sup> that a colloidal

<sup>4</sup> J. W. McBain and W. J. Jenkins, *T.*, 1922, **121**, 2325.

<sup>5</sup> (Miss) M. H. Norris, *ibid.*, 2161.

<sup>6</sup> C. S. Salmon, *ibid.*, 711.

<sup>7</sup> J. W. McBain and A. J. Burnett, *ibid.*, 1320.

solution, in which true reversible equilibria subsist, behaves as a single phase towards other phases with which it is in equilibrium.

On the other hand, for equilibria within the colloidal solution, it seems to behave as a multiphase system having one more degree of freedom than that which would be assigned to it by the ordinary phase rule.

H. M. DAWSON.

## INORGANIC CHEMISTRY.

THE study of radioactivity, isotopy, and atomic constitution has assumed such importance that a separate Report is now devoted to these developments of inorganic chemistry, and atomic constitution is here discussed solely from the stand-point of valency and the ordinary chemistry of the elements. Nevertheless, the bulk of orthodox inorganic chemical work, including as such those cases in which the application of physical methods is of interest for the results attained rather than for the methods employed, is so great that the Report can only be kept within the prescribed limits by ruthless economy of words and omission of much interesting material. An effort has been made, however, to report precisely, rather than to comment on, as much as possible of the work deemed to be of general interest to chemists.

### *Atomic Theory.*

Langmuir has deduced the types of valency, and its numerical values, for most elements by a method simpler than that formerly employed,<sup>1</sup> and, on the basis of the electron theory of chemistry, Sir J. J. Thomson<sup>2</sup> has attributed structures to the unit cells of elements according to their valency, and has calculated therefrom values for bulk-modulus, critical frequency, and dielectric constant which agree with experimental values. It has been found<sup>3</sup> that carbon dioxide and nitrous oxide have identical viscosities over the range 0—100°, and it is inferred that their molecular dimensions are the same, in agreement with Langmuir's view that both molecules have the same arrangement of the outer electrons.

The principle of induced alternate polarity of atoms, previously applied to explain many properties of organic compounds, has now been derived simultaneously and independently by Lapworth<sup>4</sup> and by Kermack and Robinson,<sup>5</sup> as a necessary consequence of the electron theory. It is perhaps important to observe that in both

<sup>1</sup> I. Langmuir, *Science*, 1921, **54**, 59; *A.*, ii, 137.

<sup>2</sup> Sir J. J. Thomson, *Phil. Mag.*, 1922, [vi], **43**, 721; *A.*, ii, 355.

<sup>3</sup> C. J. Smith, *Proc. Physical Soc.*, 1922, **34**, 155; *A.*, ii, 549.

<sup>4</sup> A. Lapworth, *T.*, 1922, **121**, 416.

<sup>5</sup> W. O. Kermack and R. Robinson, *ibid.*, 427.

cases it is found desirable to postulate union of atoms, not only by the normal "single" or "double" bond, consisting in the sharing by adjacent atoms of two or four electrons, respectively, but also by the sharing of one or three electrons. A bond of three electrons has already been proposed as affording the most rational expression of the constitution of benzene, and a single electron bond has been supposed probable,<sup>6</sup> so that there is no special difficulty in accepting the variation of the Lewis-Langmuir hypothesis. Thus among the elements of the First Period this theory continues to prove adequate.

Difficulties begin with sodium and increase among the heavier elements, where it becomes evident that the usual hypothesis is at best no more than a first approximation to the truth about atomic constitution, accounting well enough for the broad similarities within and differences between the various groups, but failing to give, for example, as any hypothesis pretending to finality must give, a theoretical basis for the detailed differences observed within each group. Reviewing such differences, one cannot escape the conclusion that chemical properties are determined, not by the outer electrons alone, but by the atomic constitution as a whole; and if this is so, the assumption, now general, that the chemical properties of isotopes are identical, whilst probably true or very nearly true for the heavier elements, may not hold for the lighter elements. It is thus important to consider the several attempts which have been made to amend the original hypothesis.

From a consideration of emission spectra, Bohr has developed a dynamic theory of the structure of the heavier elements, postulating eccentric orbits for certain electrons (which thus belong, in a sense, to more than one level in the atom), and irreconcilable with any conception of sharply separated shells of electrons,<sup>7</sup> which accounts for the colour (in compounds), paramagnetism, and relative complexity of spectra of the elements and is strongly supported by recent work upon the X-ray spectra.<sup>8</sup> Measurements of the intensity of reflection of X-rays per unit volume of the units constituting crystalline sodium chloride<sup>9</sup> may be interpreted as showing the existence in successive shells, counting outwardly, of 7 and 3 electrons in the sodium atom, and of 10, 5, and 3 electrons in the chlorine atom; or, alternatively, give for the variation of electron density with distance from the centre of each atom values which agree well with those calculated for an atom of the type proposed by

<sup>6</sup> Sir J. J. Thomson, *Phil. Mag.*, 1921, [vi], **41**, 538; *A.*, ii, 279.

<sup>7</sup> N. Bohr, *Z. Physik*, 1922, **9**, 1; *Nature*, 1921, **108**, 208; *A.*, ii, 363, 277.

<sup>8</sup> D. Coster, *Phil. Mag.*, 1922, [vi], **43**, 1070; **44**, 546; *A.*, ii, 491, 677.

<sup>9</sup> W. L. Bragg, R. W. James, and C. H. Bosanquet, *ibid.*, 1922, **44**, 433; *A.*, ii, 703.



Bohr; but appear to show clearly that there is not in either atom of sodium chloride a shell of eight electrons.

From the chemical point of view come attempts to bring the static hypothesis into closer accord with the facts by modifying Langmuir's fourth postulate. Bury's modification<sup>10</sup> reads: "The maximum number of electrons in each shell or layer is proportional to the area of its surface; thus successive layers can contain 2, 8, 18, and 32 electrons. Groups of 8 and 18 electrons in a layer are stable, even when that layer can contain a larger number of electrons. The maximum number of electrons in the outer layer of an atom is 8: more than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18 or from 18 to 32, there occurs a transition series of elements which can have more than one structure." This leaves unchanged the structures assigned by Langmuir to the elements of the First Period, but gives to all succeeding elements new structures which are in better accord with Bragg's atomic diameters and satisfactorily explain many chemical properties, for example, the similarities and differences in the triplets of Group VIII and the existence and characters of the rare earths. It seems significant, too, that Bury's structures for the inert gases are similar to those deduced by Bohr from the emission spectra. The argument of the paper cannot be reproduced in abstract and those interested will find that the original paper repays careful study. It has since been shown<sup>11</sup> that Bury's structures afford probabilities of complexity of spectra in general agreement with the observed numbers of lines for many elements.

Another alternative disposition of electrons (2 : 8 : 18 : 32 : 18 : 8 instead of Langmuir's 2 : 8 : 8 : 18 : 18 : 32) has been suggested by Dauvillier,<sup>12</sup> as a result of investigations of the *L*- and *K*-series lines in the X-ray spectra of a number of the heavier metals; and he too supposes that chemical properties are in part dependent on the internal electrons, and that inner electron shells may be incomplete. Regarding the "atomic radius" as the distance from the centre to an electron group in the valency shell, it has been shown that the distance between atomic centres is often less than the sum of the atomic radii: a number of causes may be adduced to explain the fact, among which the conception of bonds of more than one electron and the possibility of more than one arrangement of electrons within the atomic sphere<sup>13</sup> are of interest, as they have already been

<sup>10</sup> C. R. Bury, *J. Amer. Chem. Soc.*, 1921, **43**, 1602; *A.*, ii, 43.

<sup>11</sup> H. S. King, *ibid.*, 1922, **44**, 323; *A.*, ii, 277.

<sup>12</sup> A. Dauvillier, *J. Phys. Radium*, 1922, [vi], **3**, 154, 221; *Compt. rend.*, 1921, **173**, 1077; *A.*, ii, 559, 678, 43.

<sup>13</sup> M. L. Huggins, *Physical Rev.*, 1922, **19**, 346; *A.*, ii, 634.

supposed, on quite other grounds, to be possible. The suggestion is made that, in the second and third shells, the fifth and subsequent electrons pair with the first four to give a tetrahedral arrangement of pairs, and that the forces causing pairing result, in the case of the heavier elements, in the formation of triplets of electrons in the inner shells.<sup>14</sup>

This stimulating clash of theories evidently arises in part because chemical phenomena can best be interpreted by a static conception of the atom whilst physical evidence demands a dynamic conception. Therefore special interest attaches to the suggestion made by Sir Oliver Lodge<sup>15</sup> that these views might be reconciled were chemical union attributed, not to electrical attraction between the atoms, but to interlacing of the stationary magnetic fields which must accompany rapidly revolving electrons. Theories of magnetism clearly tend to assume a form favourable to such an hypothesis;<sup>16</sup> and to the connexion between chemical constitution and magnetic properties in compounds, developed chiefly by Pascal (whose recent work confirms the usual view of the constitution of the acids of sulphur, phosphorus, and arsenic),<sup>17</sup> is given new significance by experiments showing that ferro-magnetism is increased in iron and actually imparted to manganese by fusion in hydrogen, whilst the magnetic susceptibility of palladium is reduced by the adsorption of hydrogen. These phenomena may be explained by the assumption that the entry of hydrogen into the electron system of the metal produces a new system corresponding with the element of next higher atomic number, in the case of manganese, iron; in that of palladium, silver.<sup>18</sup>

### *Atomic Weights.*

*Glucinum.*—Basic glucinum acetate, prepared from the technical carbonate, was recrystallised from glacial acetic acid until free from iron, sublimed, and converted into nitrate, which was dissolved in ammonium carbonate. Glucinum carbonate precipitated from this solution was calcined to oxide, and this, by ignition with carbon in a current of chlorine, gave the pure chloride, which was collected and weighed with exclusion of water. The ratios  $\text{GlCl}_2 : 2\text{Ag}$  and

<sup>14</sup> M. L. Huggins, *Science*, 1922, **55**, 459; *J. Amer. Chem. Soc.*, 1922, **44**, 1841; *A.*, ii, 632, 744.

<sup>15</sup> Sir O. Lodge, *Nature*, 1922, **110**, 341; see also W. Hughes, *ibid.*, 1922, **110**, 37; *A.*, ii, 701, 632.

<sup>16</sup> For a useful summary, see A. E. Oxley, *Nature*, 1923, **111**, 54.

<sup>17</sup> P. Pascal, *Compt. rend.*, 1921, **173**, 712; 1922, **174**, 457, 1698; *A.*, 1921, ii, 692; 1922, ii, 285, 564.

<sup>18</sup> A. E. Oxley, *Proc. Roy. Soc.*, 1922, [*A*], **101**, 264; *A.*, ii, 469.

$\text{GICl}_2 : 2\text{AgCl}$  were determined in the usual manner, the mean result of all analyses being the value  $\text{G} = 9.018$ ,<sup>19</sup> appreciably lower than the accepted value  $\text{G} = 9.1$ .

**Boron.**—By the methods used in the foregoing determination, the same authors<sup>20</sup> have measured the ratios  $\text{BCl}_3 : 3\text{Ag}$  and  $\text{BCl}_3 : 3\text{AgCl}$ , three samples of purified boron trichloride giving the mean values  $\text{B} = 10.840$ ,  $10.818$ , and  $10.825$ , respectively. The first value is rejected for discordance and the rounded mean of the latter two values,  $\text{B} = 10.82$ , is taken.

Baxter and Scott<sup>21</sup> reduced boric oxide with excess of magnesium, extracted with hydrochloric or hydrobromic acid, and treated the resulting boron at  $700^\circ$  with chlorine or with argon saturated with bromine vapour. The samples of chloride or bromide thus prepared were freed from excess of halogen and repeatedly distilled through Hempel fractionating columns in evacuated glass apparatus. Each then gave, when compared with silver in the usual way, the value  $\text{B} = 10.83 \pm 0.01$ . These results, differing by no more than 1 part in a thousand, are a great improvement on those formerly available, and accord much better with the isotope ratio determined by Aston than, for example, the value  $\text{B} = 10.900$  found by Smith and van Haagen.<sup>22</sup>

**Yttrium.**—Yttria, prepared from Norwegian gadolinite and purified by a rigorous and prolonged process of fractional crystallisation (as bromate) and fractional precipitation, converted into chloride and titrated with weighed silver in the usual way gave, as the mean of twenty-one values varying from  $88.97$  to  $89.08$ , the value  $\text{Yt} = 89.03$ .<sup>23</sup>

**Lanthanum.**—The low value,  $\text{La} = 138.91$ , found by Baxter, Tani, and Chapin,<sup>24</sup> has been confirmed by determination of the ratio  $\text{LaCl}_3 : 3\text{Ag}$  using spectroscopically pure lanthanum chloride. Ten experiments gave for the atomic weight extreme values of  $138.84$  and  $138.97$ , with a mean  $\text{La} = 138.89$ .<sup>25</sup> It seems clear, therefore, that the international figure,  $\text{La} = 139.0$ , is too high.

Some work has been recorded on measurement of atomic weights

<sup>19</sup> O. Hönigschmid and L. Birckenbach, *Ber.*, 1922, **55**, [B], 4; *A.*, ii, 214.

<sup>20</sup> *Anal. Fis. Quím.*, 1922, **20**, 167; *A.*, ii, 641.

<sup>21</sup> G. P. Baxter and A. F. Scott, *Science*, 1921, **54**, 524; *A.*, ii, 285.

<sup>22</sup> E. F. Smith and W. K. van Haagen, *Carnegie Inst. Pub.*, 1918, **267**, 1; *A.*, 1920, ii, 247.

<sup>23</sup> H. C. Fogg and C. James, *J. Amer. Chem. Soc.*, 1922, **44**, 307; *A.*, ii, 297.

<sup>24</sup> G. P. Baxter, M. Tani, and H. C. Chapin, *ibid.*, 1921, **43**, 1080; *A.*, 1921, ii, 454.

<sup>25</sup> B. S. Hopkins and F. H. Driggs, *ibid.*, 1922, **44**, 1927; *A.* ii, 770.

by physical methods. Forty-five determinations gave a mean value of  $1.42897 \pm 0.00007$  grams for the weight of the litre of oxygen at  $0^\circ$  and 760 mm. in latitude  $45^\circ$ , in close agreement with other recent work on this constant but less by 0.00008 gram than the accepted value.<sup>26</sup> Recalculation from the known density of hydrogen bromide, using the new value for oxygen, gives  $\text{Br} = 79.927$ .<sup>27</sup>

Determinations of the normal density and compressibility of carbon dioxide and ethylene<sup>28</sup> give values for the atomic weight of carbon, 11.998 and 12.000, respectively, appreciably lower than the international value,  $\text{C} = 12.05$ , but in better accord with atomic theory; and the gravimetric determinations of Richards and Hoover have been criticised.<sup>29</sup> On the other hand, a strong protest has been entered<sup>30</sup> against such use of atomic weights derived from gas densities in criticism of "chemical" atomic weights, and supported by proof<sup>31</sup> that the proportion of impurities in atomic weight silver and iodine is very much smaller than has been alleged.<sup>32</sup>

### *Chemical Reaction.*

Before proceeding to deal with individual elements in Group order, consideration must be given to certain results which cannot be placed in any definite category (unless we invoke the hard-pressed word catalysis) and yet are clearly of fundamental significance.

Baker has extended the experiments previously reported.<sup>33</sup> Pure liquids were sealed up in Jena-glass flasks with pure phosphoric oxide and after lapse of time were opened to atmospheric pressure through dry mercury and gradually heated, precaution being taken to avoid superheating: the temperature of steady ebullition was taken as the boiling point with the results given in the table: <sup>34</sup>

<sup>26</sup> E. Moles, *J. Chim. physique*, 1921, **19**, 100; E. Moles and F. González, *Anal. Fis. Quím.*, 1922, **20**, 72; E. Moles and M. Crespi, *ibid.*, 190; *A.*, ii, 141, 497, 636.

<sup>27</sup> E. Moles, *J. Chim. physique*, 1921, **19**, 135; *A.*, ii, 140.

<sup>28</sup> Ph. A. Guye and T. Batuecas, *Helv. Chim. Acta*, 1922, **5**, 532; T. Batuecas, *ibid.*, 544; *A.*, ii, 617, 618.

<sup>29</sup> E. Moles, *Anal. Fis. Quím.*, 1921, **19**, 255; *A.*, ii, 51.

<sup>30</sup> G. P. Baxter, *J. Amer. Chem. Soc.*, 1922, **44**, 595; *A.*, ii, 370.

<sup>31</sup> G. P. Baxter and L. W. Parsons, *ibid.*, 577; G. P. Baxter, *ibid.*, 1922, **44**, 591; *A.*, ii, 376, 377.

<sup>32</sup> P. A. Guye and F. E. E. Germann, *Compt. rend.*, 1914, **159**, 225; *A.*, 1914, ii, 727.

<sup>33</sup> H. B. Baker and Muriel Baker, *T.*, 1912, **101**, 2339.

<sup>34</sup> H. B. Baker, *ibid.*, 1922, **121**, 568.

	Period of drying (years).	Original boiling point.	New boiling point.	Rise in boiling point.
Bromine .....	8	63°	118°	55°
Mercury .....	9	358	420—425	62
Hexane .....	8½	68·4	82	14
Benzene .....	8½	80	106	26
Carbon disulphide ...	1+27	49·5	80	30
„ tetrachloride...	9	78	112+	34
Ethyl ether .....	9	35	83	48
Methyl alcohol .....	9	66	120+	54
Ethyl alcohol .....	9	78·5	138	60
Propyl alcohol .....	9	95	134	39

These large differences of boiling point are undoubtedly real. The mercury maintained at 360° for thirty minutes did not boil and gave only a trace of condensate above the liquid: the hexane was transferred to another flask, not specially dried, and still boiled at 81°: water could be boiled through the benzene with only slow evaporation of the latter: and the ether at 20° had a vapour pressure of 374 mm. only, as against the normal value of 442 mm. The liquids recover their normal boiling points on exposure, even to air dried with sulphuric acid and phosphoric oxide; benzene slowly, ethyl ether and the three alcohols very rapidly.

Comparative experiments with dried and undried bromine, benzene, hexane, and nitrogen tetroxide showed that the capillary rise increased steadily during drying to a value which indicates an increase of molecular weight to 1·5—3·0 times that for the normal liquids. These results clearly support the earlier hypothesis that drying shifts the equilibrium between normal and associated molecules; possibly because absence of water hinders or inhibits dissociation, as it is known to do in the case of certain vapours, and has no effect or a smaller effect on the opposing association. If, as is usually supposed, the degree of association of a liquid is increased by lowering of temperature, information as to whether association is stopped or merely hindered might be obtained by ascertaining the ultimate effect of drying different specimens of the same liquid maintained at widely different temperatures throughout the whole period of drying. It has been shown, rather unexpectedly, that in benzene, carbon tetrachloride, carbon disulphide, ether, bromine, sulphur dioxide, and nitrogen trioxide, drying produces no change in volume as great as 1 part in 10,000.

Thermometers suspended in the vapour from dry hexane and benzene, boiling at 82° and 106°, respectively, showed temperatures of 68·4° and 80°, the boiling points of the normal liquids; a very curious result. Smits had previously suggested<sup>35</sup> that, supposing internal change to be inhibited by drying, fractional distillation

<sup>35</sup> A. Smits, *Z. physikal. Chem.*, 1922, **100**, 477; *A.*, ii, 358.

should result in a separation of the normal and associated liquids, and later experiments<sup>36</sup> have shown that if a specimen of dried benzene is distilled over completely, the temperature of a thermometer suspended in the vapour shows a steady rise, indicating that fractional distillation does, in fact, occur.

Apparently, similar changes may take place in the solid state, preliminary experiments having shown that the melting points of sulphur and iodine, originally  $112.5^{\circ}$  and  $114^{\circ}$ , are, after nine years' drying,  $117.5^{\circ}$  and  $116^{\circ}$ , respectively.

It has been found<sup>37</sup> that the reactivity of ammonia, measured by the expansion at constant temperature resulting from its partial dissociation in contact with an activated platinum wire heated by a definite current for a definite time, is the same for ammonia obtained by slow escape from a commercial cylinder of liquid ammonia, by heating aqueous ammonia and drying the gas with quicklime, or by liquefying either preparation and allowing it to evaporate isothermally at its boiling point. Under the same conditions, ammonia allowed to escape very rapidly from a cylinder had a much lower reactivity, and it is concluded that an "inactive" phase of ammonia has thus been obtained which contains more molecules of the type characteristic of liquid ammonia<sup>38</sup> than are normally present in the "active" phase, and that the existence of such active and inactive phases explains the chemical inactivity of dried gases and supports the radiation theory of chemical reactivity.<sup>39</sup>

It may be suggested, however, that the experimental results will bear a simpler, if less significant, interpretation. It is known that ordinary commercial ammonia, dried over lime, contains about 1 per cent. of water,<sup>40</sup> and that rapid, irreversible distillation such as may occur by free discharge of gas from a cylinder of liquid is a very effective means of separating the constituents even of a constant-boiling mixture,<sup>41</sup> so that the gas thus obtained may well be considerably drier than that in real equilibrium with the cylinder liquid. Baly has found that addition of water vapour to ordinary ammonia increases its reactivity, drying certainly decreases its reactivity, and so the greater dryness of the "inactive" form would appear to be capable of explaining the whole of the observations, including the "recovery" of the gas in cylinders on standing (by

<sup>36</sup> H. B. Baker, private communication.

<sup>37</sup> E. C. C. Baly and H. M. Duncan, *T.*, 1922, **121**, 1008.

<sup>38</sup> The "liquidogen" molecules of Traube, *Ann. Physik*, 1902, [iv], **8**,

<sup>39</sup> E. C. C. Baly, *Phil. Mag.*, 1920, [vi], **40**, 15; *Trans. Faraday Soc.*, 1922, **17**, 588; *A.*, ii, 628.

<sup>40</sup> See, e.g., A. G. White, *T.*, 1922, **121**, 1688.

<sup>41</sup> See, e.g., K. S. Mulliken, *J. Amer. Chem. Soc.*, 1922, **44**, 2389; *A.*, 1923, ii, 31.

acquisition of the equilibrium content of water vapour), identity of slowly released cylinder gas with laboratory preparations dried by lime, recovery of "inactive" gas in the experimental tube when the wire is heated at 200° (release of adsorbed water from the wire or walls), and the increase in reactivity of "inactive" ammonia with increase of temperature of the wire (the five pairs of figures given show that twenty seconds' heating with currents of 4.00, 4.10, 4.25, 4.35, and 4.50 amps. produces decomposition in the ratios active/inactive = 2.18, 1.76, 1.60, 1.46, and 1.35, respectively).

The "activation" of chlorine by light, a subject of much past controversy, has been reaffirmed. A rigid series of experiments <sup>42</sup> proves that when chlorine is exposed to sunlight or intense ultra-violet light and mixed with hydrogen in the dark, reaction occurs immediately on exposure of the mixture to the light of two 100-watt tungsten lamps, whilst with chlorine not so insulated reaction is delayed by the known "induction period" of about two minutes. The effect of insolation persists in the dark for three hours, but is diminished after twenty-four hours and disappears after several days. An equally rigorous series of experiments shows that chlorine exposed to the light of a 3000-watt Bovic quartz mercury lamp or to a high tension discharge will not react with hydrogen in the dark even when the interval between insolation and mixing is only 0.01 second, so that any explanation of activation in terms of the formation of a triatomic or other active form of chlorine seems improbable.

A globule of fused calcium chloride between two copper wires shows great decrease in resistance in presence of a trace of moisture, and use of this device as a "detector" has shown <sup>43</sup> that pure hydrogen reacts with copper oxide at a definite and reproducible temperature, which is lowered some 20° if the hydrogen first passes over platinised asbestos. Similar results were obtained with hydrogen and sulphur, formation of hydrogen sulphide (detected by lead acetate paper) occurring at a lower temperature if the hydrogen first passed over palladium black. The activated hydrogen was found to be ionised, but only to an extent considered altogether insufficient to explain reaction; and the persistence of the phenomenon when glass wool was interposed between the platinised asbestos and copper oxide and the absence of any change in refractive index by activation or increase of volume on decay seem to show that the observed effects cannot be attributed to monatomic or triatomic hydrogen. The explanation advanced is that the internal

<sup>42</sup> G. L. Wendt, R. S. Landauer, and W. W. Ewing, *J. Amer. Chem. Soc.*, 1922, **44**, 2377; *A.*, 1923, ii, 22.

<sup>43</sup> P. Anderson, *T.*, 1922, **121**, 1153; see also, R. N. Pease and H. S. Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2179; *A.*, ii, 148.

energy of the hydrogen molecules is increased by contact with the platinum or palladium : this should result, presumably, in a lowering of the temperature of the metal, and the explanation might thus be tested experimentally.

Lastly, reference may be made to the mysterious variation observed<sup>44</sup> in the rate of decomposition of mercuric fulminate in a vacuum at 80°, which seems to bear some resemblance to the foregoing unexplained phenomena.

### *The Inert Gases.*

A spectrophotometric method has been developed for the estimation of krypton and xenon in admixtures with argon.<sup>45</sup> Positive-ray analysis of the residues from a thousand tons of liquid air has given evidence of new constituents of the atmosphere with molecular weights 163 and 260 ; but the observed lines may be due to diatomic molecules of xenon and krypton.<sup>46</sup>

Precise determinations show that the solubility of helium has not, as was supposed, a minimum at 20°.<sup>47</sup> A detailed account of the distribution, sources, and chemical composition of helium-bearing natural gases has been published.<sup>48</sup>

Anderson has shown<sup>49</sup> that in the explosion of metallic wires by heavy condenser discharges a temperature of some 20,000° is attained in the wire in 1/300,000 second. It is now reported that thin tungsten wires exploded in this way yield gas which when obtained in a vacuum shows the helium spectrum, and if obtained in an atmosphere of pure carbon dioxide and measured after absorption of the latter in alkali has, as the mean of twenty-one experiments, a volume which corresponds to an amount of helium about 25 per cent. of the weight of tungsten taken.<sup>50</sup> This result, if confirmed, would appear to be the first case of atomic decomposition by artificial means.

### *Group I.*

Active hydrogen<sup>51</sup> has been prepared in the Siemens ozoniser, using both induction coil discharge and a Tesla discharge of much higher frequency and voltage, and also by passing pure hydrogen

<sup>44</sup> R. C. Farmer, *T.*, 1922, **121**, 174.

<sup>45</sup> C. Moureu and A. Lepape, *Compt. rend.*, 1922, **174**, 908; *A.*, ii, 394.

<sup>46</sup> Sir J. J. Thomson, *Proc. Roy. Soc.*, 1922, [A], **101**, 290; *A.*, ii, 565.

<sup>47</sup> H. P. Cady, H. M. Elsey, and E. V. Berger, *J. Amer. Chem. Soc.*, 1922, **44**, 1456; *A.*, ii, 642.

<sup>48</sup> G. S. Rogers, *U.S. Geol. Survey, Prof. Paper*, 1921, No. **121**.

<sup>49</sup> J. A. Anderson, *Astrophys. J.*, 1920, **51**, 37.

<sup>50</sup> G. L. Wendt and C. E. Irion, *J. Amer. Chem. Soc.*, 1922, **44**, 1887; *A.*, ii, 773.

<sup>51</sup> *Ann. Reports*, 1920, **17**, 37.



over a platinum wire heated electrically at  $800^{\circ}$ , the effect in this case being probably due to the emission of positive ions. It is decomposed by contact with certain metals (Pt, Ni, Cu, Pb, Sb, Cd) and unchanged by others (Ag, Hg, Sn, Bi, Mo, Zn, Al). Definite proof was obtained that hydrogen contracts when activated and recovers its original volume on standing, and that the active form condenses to a liquid at or slightly above  $-180^{\circ}$ . A relatively slow progressive change is observed in the spectrum produced by the discharge during the activation at  $-180^{\circ}$ ,<sup>52</sup> the Balmer series giving way to the secondary line spectrum. These results, especially the evident smallness of the energy change involved in its thermionic production, support the original view that this active hydrogen is in fact triatomic hydrogen,  $H_3$  (named *hyzone*, by analogy with ozone), rather than the isotope of hydrogen, *isohydrogen*, of atomic weight 3 (containing a *single* atomic nucleus of three protons) postulated by Harkins as a unit of atomic structure and, rather unfortunately, symbolised by him as  $H_3$ .

Wood has observed<sup>53</sup> that long vacuum tubes containing hydrogen give, in the central portion, mainly the Balmer series spectrum and at the ends mainly the secondary spectrum. On closing the switch, a momentary flash of the secondary spectrum, lasting about  $1/50$  sec., is seen throughout the tube, provided that  $1/5$  sec. or more has elapsed since the previous discharge. With dry hydrogen, no Balmer series is seen unless a momentary heavy condenser discharge is passed. Gas drawn by a pump from the central portion of the tube and caused to impinge upon fractured glass surfaces (or some metals, oxides, and other substances), raises them to incandescence.<sup>54</sup> The explanation advanced is that molecular hydrogen (to which the secondary spectrum is attributed) is dissociated by the discharge to form atomic hydrogen (believed to be the source of the Balmer spectrum), the incandescence of solids being due to their acting as catalysts for the exothermic recombination of the atoms.

Clearly the phenomena observed by Wendt and by Wood are very intimately related, but further experiment is necessary to decide finally which interpretation is correct, although Wendt's seems more probable. There is a concurrence of opinion that the "clean-up" of hydrogen and nitrogen in discharge tubes is due to chemical changes.<sup>55</sup> Evidence has been obtained that active

<sup>52</sup> G. L. Wendt and R. S. Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 510; *A.*, ii, 369.

<sup>53</sup> R. W. Wood, *Phil. Mag.*, 1921, [vi], **42**, 729; *A.*, 1921, ii, 665.

<sup>54</sup> R. W. Wood, *Proc. Roy. Soc.*, 1922, [A], **102**, 1; *A.*, ii, 759.

<sup>55</sup> F. H. Newman, *Phil. Mag.*, 1922, [vi], **44**, 215; *Nature*, 1922, **109**, 749; G. L. Wendt, *ibid.*, 749; *A.*, ii, 546, 639, 639.

modifications of hydrogen and nitrogen are produced also by the action of  $\alpha$ -rays.<sup>56</sup>

Measurement of the dissociation tensions has shown that lithium hydride is the most stable of all the alkali and alkaline-earth hydrides, those of calcium, strontium, and barium decreasing in stability in the order named.<sup>57</sup> X-Ray photographs of lithium hydride show a structure similar to that of sodium chloride, with positive lithium-ions and negative hydrogen-ions,<sup>58</sup> and the view that metallic hydrides are true salts, in which hydrogen acts as a halogen, is vindicated also by very ingenious and skilful experiments proving that electrolysis of a solution of calcium hydride in a fused eutectic mixture of potassium and lithium chlorides gives hydrogen at the *anode* in the quantity required by Faraday's law.<sup>59</sup>

Pure hydrogen peroxide is diamagnetic to a greater extent than water and therefore does not appear to contain the molecular linking characteristic of molecular oxygen: its solubility in alcohol is 18 per cent. and in ether 1 per cent.; it is insoluble in pure dry benzene. Curves of solubility for sodium chloride, sodium nitrate, and sugar in hydrogen peroxide are generally similar to those for the same substances in water and indicate a similar degree of ionisation of the salts. The curve for sodium sulphate in hydrogen peroxide differs materially from that in water, owing to the formation of the compound  $\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2$ . The halogen hydrides are apparently insoluble in the peroxide, but are oxidised thereby; and the halogens are much less soluble than in water. Investigation of the freezing-point curve for the system  $\text{NH}_3\text{--H}_2\text{O}_2$  up to a concentration of 60 per cent. of ammonia shows the existence of one compound only,  $\text{NH}_3 \cdot \text{H}_2\text{O}_2$ , m. p.  $24.5^\circ$ , which can be prepared also by the action of ammonia on the peroxide in anhydrous ether. Hydrogen peroxide is quite stable in the absence of water, but its decomposition is, of course, autocatalytic.<sup>60</sup>

Lithium nitrate, with a little water, is a good absorbent for ammonia, and the resulting liquid, unlike those produced with ammonium nitrate or thiocyanate, has no corrosive action on steel or iron.<sup>61</sup>

Fused caustic soda contains about 1.1 per cent. of water, which can only be removed by heating at  $500^\circ$  in a vacuum. The action

<sup>56</sup> F. H. Newman, *Phil. Mag.*, 1922, [vi], 43, 455; *A.*, ii, 279.

<sup>57</sup> F. Ephraim and E. Michel, *Helv. Chim. Acta*, 1921, 4, 900; *A.*, ii, 58.

<sup>58</sup> J. M. Bijvoet and A. Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, 25, 26; *A.*, ii, 569.

<sup>59</sup> D. C. Bardwell, *J. Amer. Chem. Soc.*, 1922, 44, 2499; *A.*, 1923, ii, 20.

<sup>60</sup> O. Maass and W. H. Hatcher, *ibid.*, 2472; *A.*, 1923, ii, 21.

<sup>61</sup> R. O. E. Davis, L. B. Olmstead, and F. O. Landstrum, *ibid.*, 1921, 43, 1575, 1580; *A.*, ii, 56, 49.

upon iron, nickel, and copper of fused caustic soda, with and without the addition of 5—10 per cent. of sodium peroxide, has been studied at 350—720°; the results are very complex and interesting, many definite crystalline products having been obtained. That obtained from iron forms transparent red hexagonal crystals, stable to boiling water or aqueous caustic soda and to cold dilute mineral acids, but apparently decomposing when kept; analysis gave the composition  $\text{Na}_2\text{Fe}_3\text{O}_6$ , and there is some evidence that a similar compound is formed with nickel.<sup>62</sup>

Sodium sulphate tetrahydrate,  $\text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , otherwise unknown, has been shown to exist in mixed crystals with sodium chromate.<sup>63</sup>

Experience gained in the preparation of free tetraethylammonium has led to the preparation of free ammonium in about a 50 per cent. yield by the addition of a 1.8 per cent. solution of potassium in liquid ammonia to a 1 per cent. ammonia solution of ammonium chloride at -70°.<sup>64</sup>

Rubidium bromate, prepared from the pure carbonate and bromic acid and recrystallised, forms, like caesium bromate, small hexagonal crystals resembling cubes, m. p. 430°, and sparingly soluble in water.<sup>65</sup>

Measurement over a range of temperatures of the dissociation pressures of hydrated cupric alkali sulphates, of the type  $\text{CuSO}_4 \cdot \text{M}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , showed the stability at any given temperature to increase in the order K, Rb, Tl,  $\text{NH}_4$ , Cs; and it is inferred that the basicity of the corresponding hydroxides increases in the same order.<sup>66</sup>

Excess of hydrogen peroxide gives with cold solutions of sodium copper carbonate a gelatinous, yellowish-brown precipitate having an oxygen : copper ratio between Cu :  $1\frac{1}{2}\text{O}$  and Cu : 2O, thus affording fresh evidence for the existence of an unstable peroxide,  $\text{CuO}_2$ .<sup>67</sup> The action of potassium persulphate on cuprous hydroxide in presence of barium hydroxide below 0° is said to give the oxide  $\text{Cu}_2\text{O}_3$  which, whilst an oxidising agent, is apparently not peroxidic.<sup>68</sup>

Cuprous sulphide is formed by the action of sulphur on cuprous chloride.<sup>69</sup> Cupric sulphide on oxidation by air yields free sulphur

<sup>62</sup> T. Wallace and A. Fleck, *T.*, 1921, **119**, 1839.

<sup>63</sup> T. W. Richards and W. B. Meldrum, *J. Amer. Chem. Soc.*, 1921, **43**, 1543; *A.*, ii, 54.

<sup>64</sup> H. H. Schlubach and F. Ballauf, *Ber.*, 1921, **54**, [B], 2825; *A.*, ii, 55.

<sup>65</sup> H. D. Buell and C. R. McCrosky, *J. Amer. Chem. Soc.*, 1921, **43**, 2031 *A.*, ii, 146.

<sup>66</sup> R. M. Caven and J. Ferguson, *T.*, 1922, **121**, 1406.

<sup>67</sup> J. Aldridge and M. P. Applebey, *ibid.*, 238.

<sup>68</sup> G. Scagliarini and G. Torelli, *Gazzetta*, 1921, **51**, ii, 225; *A.*, ii, 68.

<sup>69</sup> F. W. Pinkard and W. Wardlaw, *T.*, 1922, **121**, 1300.

if freshly precipitated, but only cupric sulphate and thiosulphate if preserved for some hours before exposure to oxygen; the existence of two modifications, formulated as  $\text{Cu}^{\text{II}}\text{S}$  and  $\text{Cu}^{\text{I}}\text{S}_2$ , is inferred.<sup>70</sup>

The corrosion of copper by ammonium nitrate and ammonia has been found to yield cupric tetrammine nitrate and nitrite, and the preparation of the latter compound from basic cupric nitrite and ammonia is described. Dry cupric tetrammine nitrate is remarkably stable, retaining its ammonia at  $120^\circ$  in a vacuum, but exploding at  $212^\circ$ : the nitrite loses ammonia at  $95\text{--}100^\circ$  in air, forming the diammine nitrite,  $\text{Cu}(\text{NH}_3)_2(\text{NO}_2)_2$ .<sup>71</sup>

A strong solution of sodium persulphate (preferable to the potassium salt because of its greater solubility) acts on finely divided crystalline silver or concentrated aqueous silver nitrate to give a black peroxide which, in the latter case, gave an atomic ratio O/Ag as high as 1.295 and therefore was possibly impure  $\text{Ag}_3\text{O}_4$ .<sup>72</sup>

In sharp contrast with a number of doubtful or negative results,<sup>73</sup> Hartung, using a Steele and Grant type B quartz micro-balance<sup>74</sup> carrying 43 mg. and sensitive to  $2 \times 10^{-5}$  mg., has shown that films of silver chloride, bromide, or iodide, formed by direct halogenation of silver films, deposited from a tartrate silvering solution on thin silica supports, are darkened on exposure to light and lose weight, in some experiments with the chloride to the extent of more than 80 per cent. of the halogen present in the salt. Decomposition was accelerated in a vacuum or by presence of ozone, and rehalogenation restored the original weight and colour.<sup>75</sup> It seems clear, therefore, that neither oxygen nor water is essential to light action on the silver halides, and that their decomposition yields metal and halogen, and not a sub-halide.

Adsorption of iodine from aqueous or alcoholic solution does not occur with pure silver iodide,<sup>76</sup> and Carey Lea's observation to the contrary was probably due to the presence of silver nitrate as an

<sup>70</sup> W. Glund, *Ber.*, 1922, **55**, [B], 952, 1760; *A.*, ii, 446, 572.

<sup>71</sup> H. Bassett and R. G. Durrant, *T.*, 1922, **121**, 2630.

<sup>72</sup> G. I. Higson, *ibid.*, 1921, **119**, 2048.

<sup>73</sup> A. G. Rabinovich, *J. Physical Chem.*, 1922, **26**, 577; C. Tubandt and G. Eschenhagen, *Z. physikal. Chem.*, 1922, **100**, 489; J. Eggert and W. Noddack, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 631; F. Weigert and W. Schöller, *ibid.*, 1921, 641; P. P. Koch and F. Schrader, *Z. Physik*, 1921, **6**, 127; *A.*, ii, 605, 346, 9, 10, 183.

<sup>74</sup> E. J. Hartung, *Phil. Mag.*, 1922, [vi], **43**, 1056; *A.*, ii, 495.

<sup>75</sup> *Idem.*, *T.*, 1922, **121**, 682.

<sup>76</sup> F. E. E. Germann and R. N. Traxler, *J. Amer. Chem. Soc.*, 1922, **44**, 460; *A.*, ii, 371.

impurity in his silver iodide. Silver perchlorate is extremely soluble in water and moderately soluble in benzene, and the three components form a remarkable system which has been studied up to the melting point of silver nitrate; silver perchlorate and water have the lowest eutectic point known for a true salt and water,  $-50.2^{\circ}$ ; and a hydrate,  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ , and a compound,  $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$ , have been isolated.<sup>77</sup> Silver bromate is dimorphous, forming tetragonal crystals below and hair-like crystals above the transition point,  $98.5^{\circ}$ ; the dry salt melts at  $308\text{--}310^{\circ}$  and is stable to light; it may advantageously be substituted for arsenious oxide as a standard in iodometry.<sup>78</sup> The existence of colourless and yellow forms of alkali silver thiosulphates is confirmed, and several new compounds of this type are described.<sup>79</sup>

A number of new, complex gold chlorides containing ammonium, rubidium, and caesium have also been prepared.<sup>80</sup> Anodic oxidation of gold in dilute sulphuric acid is shown to yield auric hydroxide.<sup>81</sup> Hydrogen sulphide in excess reacts with very dilute aqueous chloroauric acid to give pure auric sulphide, but the sulphides  $\text{Au}_2\text{S}$  and  $\text{Au}_2\text{S}_2$  could not be obtained.<sup>82</sup>

The existence of reaction limits in gold alloys previously reported<sup>83</sup> has been confirmed by electrochemical investigations,<sup>84</sup> and Tammann's explanation, although subject to criticism, still appears the most probable.<sup>85</sup>

### Group II.

A comparison of the band spectrum of glucinum with that of aluminium confirms the close similarity of atomic structure for these metals which would be anticipated from their chemical relationship.<sup>86</sup>

Glucinum hydroxide precipitated from the sulphate by ammonia is found always to contain much ammonium sulphate, which cannot

<sup>77</sup> A. E. Hill, *J. Amer. Chem. Soc.*, 1922, **44**, 1163; *A.*, ii, 555.

<sup>78</sup> J. H. Reedy, *ibid.*, 1921, **43**, 1440; *A.*, ii, 56.

<sup>79</sup> E. Jonsson, *Ber.*, 1921, **54**, [B], 2556; *A.*, ii, 57.

<sup>80</sup> E. Suschnig, *Monatsh.*, 1921, **42**, 399; *A.*, ii, 514; H. L. Wolls, *Amer. J. Sci.*, 1922, **3**, [v], 257, 315, 414; *A.*, ii, 449, 449, 514.

<sup>81</sup> F. Jirsa and O. Buryánek, *Chem. Listy*, 1922, **16**, 189; *A.*, ii, 713.

<sup>82</sup> A. Gutbier and E. Dürnwächter, *Z. anorg. Chem.*, 1922, **121**, 266; *A.*, ii, 513.

<sup>83</sup> *Ann. Reports*, 1919, **16**, 198.

<sup>84</sup> G. Tammann, *Z. anorg. Chem.*, 1921, **118**, 48, 93; 1922, **121**, 193; R. Lorenz, W. Fraenkel, and M. Wormser, *ibid.*, 1921, **118**, 231; *A.*, ii, 75, 380, 63, 21.

<sup>85</sup> G. Masing, *Z. anorg. Chem.*, 1921, **118**, 293; W. H. Creutzfeldt, *ibid.*, 1922, **121**, 25; W. Jenge, *ibid.*, 1921, **118**, 36; G. Tammann, *Z. Elektrochem.*, 1922, **28**, 36; *A.*, ii, 37, 347, 64, 255.

<sup>86</sup> L. C. Glaser, *Ann. Physik*, 1922, [iv], **68**, 73; *A.*, ii, 675.

be washed out unless the hydroxide is first dried and powdered; when thus purified and dried, it approximates closely to the composition  $\text{Gl}(\text{OH})_2$ .

The form of the  $25^\circ$ -isotherm for the system  $\text{GlSO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$  shows that over the range 27—30 per cent. of  $\text{GlSO}_4$  and 28—37 per cent. of  $(\text{NH}_4)_2\text{SO}_4$ , the solid phase is the double salt,  $\text{GlSO}_4, (\text{NH}_4)_2\text{SO}_4, 2\text{H}_2\text{O}$ ; <sup>87</sup> and solubility determinations for glucinum sulphate in water indicate that  $\text{GlSO}_4, 4\text{H}_2\text{O}$  is the only solid phase, and that the hexahydrate previously reported is not formed. <sup>88</sup>

Dilute magnesium amalgam absorbs ammonia with separation of a solid solution of magnesium hexammoniate,  $\text{Mg}(\text{NH}_3)_6$ , in mercury; <sup>89</sup> and thermal analysis of the system magnesium—mercury shows the existence of the compounds  $\text{MgHg}_2$ , with transition at  $170^\circ$  to  $\text{MgHg}$ , m. p.  $625^\circ$ ;  $\text{Mg}_3\text{Hg}_2$ , m. p.  $562^\circ$ ; and  $\text{Mg}_2\text{Hg}$ , m. p.  $580^\circ$ . <sup>90</sup>

Magnesium perchlorate has been found to form a trihydrate as well as the hexahydrate previously described: it is completely dehydrated without decomposition at  $250^\circ$ , and the anhydrous salt has a remarkable avidity for water and has been proved to be an excellent neutral drying agent, rather slower in action than phosphoric oxide but as efficient as the latter at the ordinary temperature, capable of absorbing a greater quantity of water per unit weight, and easily regenerated by heating. <sup>91</sup> Evidence is adduced for the existence of magnesium sulphate octahydrate, having a transition point to the heptahydrate at  $48.2^\circ$ . <sup>92</sup>

An improved method is given for the electrolytic preparation of dilute calcium amalgam. <sup>93</sup> Metallic calcium gives a vapour pressure curve which, by extrapolation, indicates a boiling point of  $1240^\circ$ ; but the metal used contained nearly 3 per cent. of impurity, including 1.62 per cent. of magnesium, <sup>94</sup> and it seems appropriate to repeat the protest entered in a previous Report against the use of impure or indefinite material in exact determinations. Pure calcium is found to be almost passive toward nitrogen, but the presence of more electropositive metals (K, Ba) or, better, calcium nitride favours reaction. <sup>95</sup>

<sup>87</sup> H. T. S. Britton, *T.*, 1922, **121**, 2612.

<sup>88</sup> *Idem.*, *ibid.*, 1921, **119**, 1967.

<sup>89</sup> A. C. Loomis, *J. Amer. Chem. Soc.*, 1922, **44**, 8; *A.*, ii, 294.

<sup>90</sup> R. P. Beck, *Rec. trav. chim.*, 1922, **41**, 353; *A.*, ii, 545.

<sup>91</sup> H. H. Willard and G. F. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2255; *A.*, ii, 850.

<sup>92</sup> S. Takogami, *J. Chem. Soc. Japan*, 1921, **42**, 441; *A.*, 1921, ii, 698.

<sup>93</sup> B. S. Neuhausen, *J. Amer. Chem. Soc.*, 1922, **44**, 1445; *A.*, ii, 643.

<sup>94</sup> N. B. Pilling, *Physical Rev.*, 1921, **18**, 362; *A.*, ii, 291.

<sup>95</sup> O. Ruff and H. Hartmann, *Z. anorg. Chem.*, 1922, **121**, 167; O. Ruff, *Z. physikal. Chem.*, 1922, **100**, 419; *A.*, ii, 377, 363.

The existence of solid calcium-ammonium at  $-15^{\circ}$  to  $+30^{\circ}$  is confirmed;<sup>96</sup> and new compounds of calcium chloride with 1 mol. of ammonia and of calcium bromide and iodide with 1, 2, and 8 molecules of ammonia have been prepared, and the vapour tensions of these and the known ammines determined.<sup>97</sup> The second calcium silicide previously reported and variously formulated by different workers, is now shown to be calcium monosilicide,  $\text{CaSi}$  or  $\text{Ca}_2\text{Si}_2$ .<sup>98</sup>

Strontium is completely insoluble in solid lead, but forms one compound,  $\text{Pb}_3\text{Sr}$ , m. p.  $676^{\circ}$ , which is said to form with lead a eutectic melting at the same temperature as lead.<sup>1</sup>

Reaction between nitrogen in excess and compressed mixtures of barium carbonate with wood-charcoal or graphite attains a practicable velocity at  $1300$ — $1400^{\circ}$ : in fifteen to thirty minutes at this temperature, formation of cyanide reaches a maximum of 65 per cent., which is not increased at  $1600^{\circ}$ . The primary change produces barium carbide, which then reacts with nitrogen to form cyanide; cyanamide formation is due to a secondary reaction which is facilitated by higher temperature.<sup>2</sup>

Barium sulphate dissolves in 98 per cent. sulphuric acid at  $25^{\circ}$  to the extent of 14.9 grams/100 c.c., and the solution contains barium sulphuric acid,  $\text{H}_2[\text{Ba}(\text{SO}_4)_2]$ , which can be accumulated and crystallised in the anode compartment by electrolytic transport. Barium selenic acid can be prepared in a similar manner or by crystallisation from a saturated solution of barium selenate in selenic acid.<sup>3</sup>

Thermal analysis shows the zinc-arsenic alloys to comprise two brittle compounds,  $\text{Zn}_3\text{As}_2$ , m. p.  $1015^{\circ}$ , and  $\text{ZnAs}_2$ , m. p.  $771^{\circ}$ ;<sup>4</sup> and indicates that magnesium and cadmium form one compound,  $\text{CdMg}$ , soluble in all proportions in either metal.<sup>5</sup>

Cadmium dissolves in aqueous ammonium nitrate quietly and without evolution of gas, and it has thus been proved that impurities in the metal form a net-like structure between the crystallites.<sup>6</sup>

Tests of the method previously described<sup>7</sup> for the purification of mercury by air at  $150^{\circ}$  showed that it removed lead completely

<sup>96</sup> E. Botolfsen, *Bull. Soc. chim.*, 1922, [iv], **31**, 561; *A.*, ii, 570.

<sup>97</sup> G. F. Hüttig, *Z. anorg. Chem.*, 1922, **123**, 31; *A.*, ii, 849.

<sup>98</sup> L. Wöhler and F. Müller, *ibid.*, 1921, **120**, 49; *A.*, ii, 293.

<sup>1</sup> E. Piwowarsky, *Z. Metallk.*, 1922, **14**, 300; *A.*, ii, 644.

<sup>2</sup> P. Askenasy and F. Grude, *Z. Elektrochem.*, 1922, **28**, 130; *A.*, ii, 445.

<sup>3</sup> J. Meyer and W. Friedrich, *Z. physikal. Chem.*, 1922, **101**, 498; *A.*, ii, 644.

<sup>4</sup> W. Heike, *Z. anorg. Chem.*, 1921, **118**, 264; *A.*, ii, 60.

<sup>5</sup> L. Guillet, *Rev. Met.*, 1922, **19**, 359; *A.*, ii, 570.

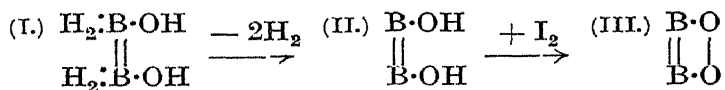
<sup>6</sup> G. Tammann, *Z. anorg. Chem.*, 1922, **121**, 275; *A.*, ii, 502.

<sup>7</sup> *Ann. Reports*, 1921, **18**, 45.

with a loss of 2 per cent. of mercury as against a loss of 3.7 per cent. when purification was effected in the usual way with nitric acid ( $d$  1.175), but that tin was not completely eliminated by fifteen hours' air treatment (loss 1.4 per cent.) or by three passages through nitric acid (loss 9.2 per cent.).<sup>8</sup> A study of the equilibrium between mercuric chloride, yellow mercuric oxide, and water at 35° shows the existence of two oxychlorides of mercury;  $\text{HgCl}_2 \cdot 2\text{HgO}$ , forming purplish-scarlet needles, and  $\text{HgCl}_2 \cdot 4\text{HgO}$ , a brownish-yellow amorphous substance which appears to form a solid solution with mercuric oxide.<sup>9</sup>

### Group III.

The potassium salt of hexahydrodioxydiboron has been isolated. Magnesium boride is extracted with dilute aqueous potassium hydroxide, the extract is concentrated in a vacuum, separated from potassium metaborate and magnesium hydroxide and further concentrated, and the residue is washed with methyl alcohol and recrystallised two or three times in a vacuum from water free from carbon dioxide. It forms slightly deliquescent, colourless crystals, easily soluble in water. The solution has an alkaline reaction, is a powerful reducing agent, and yields hydrogen when acidified and even, slowly, on exposure to atmospheric carbon dioxide; concentrated nitric acid acts upon the solid salt so vigorously that the hydrogen evolved takes fire. The salt in solution evolves 2.95 per cent. of its weight of hydrogen; the residual solution can further absorb 1 atom of iodine for each two atoms of hydrogen previously evolved; and measurements of equivalent conductivity indicate that the molecular formula is  $\text{K}_2\text{O}_2\text{B}_2\text{H}_4$ .<sup>10</sup> The properties of the salt thus confirm the earlier view<sup>11</sup> that aqueous extracts of magnesium boride contain the acid  $\text{H}_6\text{B}_2\text{O}_2$ , to which the structural formula (I) is attributed because it best represents the loss of hydrogen to form (II) and the subsequent interaction with iodine (III).



In the course of attempts to prepare complex polyborates, the pentaborates of potassium, rubidium, and thallium,  $\text{M}^{\text{I}}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ , crystallising with 8, 10, and  $8\text{H}_2\text{O}$ , respectively, have been prepared.<sup>12</sup>

Crystalline aluminium hydroxide, identical under X-ray examination with the mineral *gibbsite*, begins to decompose only at 145° and

<sup>8</sup> C. Harries and F. Evers, *Z. angew. Chem.*, 1921, **34**, 541; *A.*, 1921, ii, 698.

<sup>9</sup> S. Toda, *J. Chem. Soc. Japan*, 1922, **43**, 312; *A.*, ii, 769.

<sup>10</sup> R. C. Rây, *T.*, 1922, **121**, 1088.

<sup>11</sup> Of Travers, Rây, and Gupta.

<sup>12</sup> A. Rosenheim and F. Leyser, *Z. anorg. Chem.*, 1921, **119**, 1; *A.*, ii, 50.



at 200° still retains 8 per cent. of water, which is completely removed only at much higher temperatures. The product of dehydration at 275° adsorbs water, but does not combine with it. Alumina prepared by dehydration at 325° gives an *X*-ray pattern which indicates a structure, crystalline, but different from that of diaspor,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , or corundum; the product of calcination above 1000° gives the pattern of corundum.<sup>13</sup>

Aluminium chlorosulphoxide,  $\text{AlCl}_3 \cdot \text{SO}_2$ , is obtained by agitating powdered aluminium chloride with sulphuryl chloride for eight hours at 0—30° with rigid exclusion of water; when treated with sulphur or sulphur monochloride in sulphuryl chloride solution, it yields a crystalline precipitate of the compound  $\text{Al}_2\text{Cl}_6 \cdot \text{S}_2\text{Cl}_2$ . Both compounds are violently decomposed by water, in the latter case with separation of free sulphur, and are extremely active agents for the chlorination of organic compounds.<sup>14</sup>

It has been found that hydrochloric and sulphuric acids do not, as has been supposed, reduce thallic oxide, but dissolve it to form the corresponding thallic salts. The existence of an acid (or mixed) sulphate, with a ratio  $\text{Tl} : \text{SO}_4 = 1 : 2$ , has been confirmed; and the reduction of thallic salts by hydroxylamine, ferrous sulphate, and sodium arsenite has been found to proceed according to the equations  $\text{Tl}_2\text{O}_3 + 2\text{NH}_2 \cdot \text{OH} \rightarrow \text{Tl}_2\text{O} + 3\text{H}_2\text{O} + \text{N}_2\text{O}$ ;  $\text{Tl}_2(\text{SO}_4)_3 + 4\text{FeSO}_4 \rightarrow 2\text{Tl}_2\text{SO}_4 + 2\text{Fe}_2(\text{SO}_4)_3$ ;  $\text{Tl}_2\text{O}_3 + \text{As}_2\text{O}_3 \rightarrow \text{Tl}_2\text{O} + \text{As}_2\text{O}_5$ .<sup>15</sup> There is reason to believe that  $\text{Tl}_2\text{SO}_4$ ,  $\text{Tl}_2(\text{SO}_4)_3$  and  $5\text{Tl}_2\text{SO}_4 \cdot \text{Tl}_2(\text{SO}_4)_3$  are the only thallos-thallic sulphates which exist.<sup>16</sup>

Thermal analysis of the system  $\text{Tl}_2\text{O}-\text{B}_2\text{O}_3$  indicates the existence of thallos ortho-, meta-, and pyro-borates, the first melting at 370° with decomposition and the others melting at about 474° and 434°, respectively.<sup>17</sup> Double halides of thallium and bismuth,  $2\text{TlBr} \cdot \text{BiBr}_3$  and  $2\text{TlI} \cdot \text{BiI}_3$ , precipitated by potassium bromide or iodide from nitric acid solutions of the constituent metals, form respectively lemon-yellow and red hexagonal crystals, readily hydrolysed to thallos halide, bismuth oxyhalide, and free halogen;<sup>18</sup> and some double thiosulphates of thallium and arsenic, antimony, or bismuth, of the type  $\text{Tl}_3\text{M}(\text{S}_2\text{O}_3)_3$ ,<sup>19</sup> and complex or

<sup>13</sup> L. H. Milligan, *J. Physical Chem.*, 1922, **26**, 247; *A.*, ii, 447.

<sup>14</sup> O. Silberrad, *T.*, 1922, **121**, 1015.

<sup>15</sup> A. J. Berry, *ibid.*, 394.

<sup>16</sup> A. Benrath and H. Espenschied, *Z. anorg. Chem.*, 1922, **121**, 361; *A.*, ii, 504.

<sup>17</sup> G. Canneri and R. Morelli, *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 109; *A.*, ii, 571.

<sup>18</sup> G. Canneri and G. Perina, *Gazzetta*, 1922, **52**, i, 241; *A.*, ii, 512.

<sup>19</sup> G. Canneri, *ibid.*, 37; *A.*, ii, 378.

<sup>20</sup> V. Cuttica and A. Paciello, *ibid.*, 141; *A.*, ii, 377.

double nitrites of thallium with copper, nickel, barium, or lead,  $\text{Ti}_3[\text{Cu}(\text{NO}_2)_5]$ ;  $\text{Ti}_4[\text{Ni}(\text{NO}_2)_6]$ ;  $\text{TiNO}_2 \cdot 2\text{Ba}(\text{NO}_2)_2$ ;  $2\text{TiNO}_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$  have been described.<sup>20</sup>

A careful redetermination has been made of the densities of the oxides of six rare-earth metals (La, Pr, Nd, Sm, Eu, Gd),<sup>21</sup> and a good deal of work, which cannot usefully be summarised here, has been done on the separation of the rare-earths by basic precipitation and kindred methods,<sup>22</sup> and on the extraction of scandium from thorveitite and its purification.<sup>23</sup>

#### Group IV.

The fusion of carbon at atmospheric pressure by resistance heating of carbon rods is reported: the solidified drops of carbon and the points from which they are detached are said to consist of pure graphite.<sup>24</sup> The observation that diamond is unchanged when heated at  $1100^\circ$  in carbon dioxide but becomes covered with amorphous carbon<sup>25</sup> would, if correct, seem to afford a possible means of preparing pure carbon without possibility of contamination with hydrogen, an attempt to obtain this by decomposition of carbon monoxide at  $450^\circ$  in presence of ferric oxide having failed.<sup>26</sup>

When aqueous carbon dioxide is added to a large excess of ammonia, the anhydrous carbon dioxide immediately forms ammonium carbamate, which is sufficiently stable to permit the precipitation of the carbonate carbon dioxide as barium carbonate. This method has been applied to a study of the hydration of carbon dioxide in solutions of sodium hydroxide and sodium carbonate.<sup>27</sup>

Iron pentacarbonyl is best obtained from iron and carbon monoxide at  $200^\circ$  and 300 atm. pressure; molybdenum carbonyl, formerly supposed to be  $\text{Mo}(\text{CO})_6$ , is now found to have a Mo : CO ratio 1 : 5.2, best represented by  $\text{Mo}_5(\text{CO})_{26}$  or a similar complex formula. Two ruthenium carbonyls are obtained at 300—400 atm. pressure: one a crystalline solid of unknown composition, soluble in benzene but insoluble in alcohol or water; the other a chocolate-brown, amorphous solid,  $\text{Ru}(\text{CO})_2$ , insoluble in benzene, but soluble in

<sup>21</sup> W. Prandtl, *Ber.*, 1922, **55**, [B], 692; *A.*, ii, 379.

<sup>22</sup> W. Prandtl and J. Rauchenberger, *Z. anorg. Chem.*, 1921, **120**, 120, 311; W. Prandtl and J. Lösch, *ibid.*, 1922, **122**, 159; P. H. M.-P. Brinton and C. James, *J. Amer. Chem. Soc.*, 1921, **43**, 1397, 1446; *A.*, ii, 298, 770, 769, 62, 39.

<sup>23</sup> P. Urbain and G. Urbain, *Compt. rend.*, 1922, **174**, 1310; *A.*, ii, 504.

<sup>24</sup> E. Ryschkewitsch, *Z. Elektrochem.*, 1921, **27**, 445; 1922, **28**, 185; compare F. Sauerwald, *ibid.*, 1922, **28**, 183; *A.*, 1921, ii, 696; 1922, ii, 443.

<sup>25</sup> A. Foix, *Bull. Soc. chim.*, 1922, [iv], **33**, 678; *A.*, ii, 641.

<sup>26</sup> J. P. Wibaut, *Rec. trav. chim.*, 1922, **41**, 400; *A.*, ii, 565.

<sup>27</sup> C. Faurholt, *Z. anorg. Chem.*, 1921, **120**, 85; *A.*, ii, 272.

alcohol or water without decomposition.<sup>28</sup> The action of nitric oxide on cobalt tetracarbonyl causes evolution of carbon monoxide and yields a cherry-red liquid which has been definitely characterised as  $\text{Co}(\text{CO})_3\text{NO}$ ,  $d^{14} = 1.5126$ ; m. p.  $-1.05^\circ$ ; b. p.  $78.6^\circ$  at 760 mm. Mol. wt. (from V.D.) = 171.7 (calc.  $M = 173$ ); it decomposes slowly above  $66^\circ$ . Similar actions take place with nitric oxide and nickel pentacarbonyl or diferro nonacarbonyl, but the yields were too small to enable the composition of the products to be established.<sup>29</sup>

Pure sugar charcoal, heated with sulphur at  $400\text{--}1000^\circ$  at low pressures, yields a coke-like solid containing 2.0—3.5 per cent. of sulphur which is not extracted by toluene and is only partly oxidised by bromine water or removed by heating at  $750^\circ$  in hydrogen: this affords further evidence of the existence of stable solid sulphides of carbon.<sup>30</sup>

Investigations of the solubility in hydrofluoric acid of the varieties of silicon obtained by crystallisation from solution in molten aluminium, silver, and copper lead to the conclusion that they differ mainly in degree of subdivision and are not really allotropic forms; <sup>31</sup> a view confirmed by X-ray evidence that the structures of amorphous, graphitic, and crystalline silicon are identical.<sup>32</sup>

Sodium metasilicate is found to yield three hydrates only:  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , rhombic, m. p.  $47^\circ$ ;  $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$ , monoclinic, m. p.  $63.5^\circ$ ; and  $\text{Na}_2\text{SiO}_3 \cdot 4\text{H}_2\text{O}$ , hexagonal, m. p.  $83\text{--}85^\circ$ , other hydrates mentioned in the literature being probably mixtures of these.<sup>33</sup>

Much interesting work has been done on germanium, our previous knowledge of which was due very largely to Winkler, whose investigations were limited by lack of material. Germanium has been extracted from zinc residues containing about 0.2 per cent. of Ge by processes, described in detail in the original,<sup>34</sup> dependent on the volatility of the chloride with steam; in this way relatively large amounts of this very rare element have been obtained and are being utilised in a reinvestigation of its compounds.

Germanium dioxide is largely, but not wholly, reduced to metal by hydrogen at  $550\text{--}900^\circ$ ; the metal reacts with pure bromine,

<sup>28</sup> R. L. Mond and A. E. Wallis, *T.*, 1922, **121**, 29.

<sup>29</sup> *Idem.*, *ibid.*, 32.

<sup>30</sup> J. P. Wibaut, *Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 92; *Rec. trav. chim.*, 1922, **41**, 153; *A.*, ii, 52, 373.

<sup>31</sup> W. Manchot, *Ber.*, 1921, **54**, [B], 3107; W. Manchot and H. Funk, *Z. anorg. Chem.*, 1922, **120**, 277; **122**, 22; *A.*, ii, 144, 286, 764.

<sup>32</sup> W. Gerlach, *Physikal. Z.*, 1922, **23**, 114; *A.*, ii, 265.

<sup>33</sup> A. Erdenbrecher, *Mikrokosmos*, 1921, **15**, 55; *A.*, ii, 444.

<sup>34</sup> L. M. Dennis and J. Papish, *J. Amer. Chem. Soc.*, 1921, **43**, 2131; *A.*, ii, 150.

superficially at the ordinary temperature, completely at  $220^{\circ}$ , to form the tetrabromide, which is best purified by fractional distillation and then forms a white solid crystallising in regular octahedra, m. p.  $26.1^{\circ}$ , b. p. (corr.)  $185.9^{\circ}$ . The liquid can be supercooled to  $-18^{\circ}$  and has  $n_D^{25} = 1.6269$ ,  $d_{25}^{25} = 3.1315$ , and specific conductivity  $< 0.000078$  mhos. The tetrachloride, similarly prepared, and freed from chlorine by prolonged passage of a current of air, is a colourless liquid, b. p.  $86.5^{\circ}$  (corr.), m. p.  $-49.5^{\circ}$ ,  $n_D^{25} 1.3606$ ,  $d_{25}^{25} 1.874$ . Both compounds fume in air and are slowly decomposed by water with a characteristic crackling sound, but are unchanged by strong sulphuric acid.<sup>35</sup>

As an outcome of general investigations<sup>36</sup> on the preparation of gaseous metallic hydrides by the spark discharge and from alloys and solutions germanium hydride has been shown to have the composition  $\text{GeH}_4$  and to be free from any considerable amount of other hydrides.<sup>37</sup> By a modified form of the Marsh test, the formation and decomposition of the hydride may be used as an extremely delicate test for germanium; and it may be estimated gravimetrically by precipitation as magnesium orthogermanate,  $\text{MgGeO}_4$ .<sup>38</sup>

Stannous hydroxide, prepared by precipitating aqueous stannous chloride with sodium hydroxide or ammonia, is stable in air, wet or dry, up to  $110^{\circ}$ , dissolves in acetic acid to form stannous acetate,  $\text{Sn}(\text{C}_2\text{H}_3\text{O}_2)_2$ , has probably the formula  $3\text{SnO}_2 \cdot 2\text{H}_2\text{O}$ , and by keeping under water is converted into dark grey, crystalline stannous oxide, which is dispersed to a yellow, colloidal solution by excess of water.<sup>39</sup>

The change of  $\alpha$ -stannic acid to  $\beta$ -stannic acid is explained as due to the combination of stannic hydroxide (functioning as a base) with itself (functioning as an acid), and the theory receives support from measurements of the relative strength of the hydroxide as acid and as base considered in conjunction with the solubility of the  $\alpha$ - and  $\beta$ -forms in hydrochloric acid and caustic alkali, as to which new facts are adduced.<sup>40</sup>

The existence of lead monoxide in two forms, recently denied,<sup>41</sup> has been conclusively proven. By slow cooling, solutions of lead oxide in aqueous caustic potash yield, according to the concentration of alkali, relatively large crystals of either the stable red tetragonal

<sup>35</sup> L. M. Dennis and F. E. Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 299; *A.*, ii, 302.

<sup>36</sup> F. Paneth *et al.*, *Ber.*, 1922, **55**, [B], 769, 775; *A.*, ii, 383.

<sup>37</sup> F. Paneth and E. Schmidt-Hebbel, *ibid.*, 2615; *A.*, ii, 776.

<sup>38</sup> J. H. Müller and N. H. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 1909; *A.*, ii, 775; J. H. Müller, *ibid.*, 2493; *A.*, 1923, ii, 43.

<sup>39</sup> F. W. Bury and J. R. Partington, *T.*, 1922, **121**, 1998.

<sup>40</sup> G. E. Collins and J. K. Wood, *ibid.*, 441, 1122, 2760.

<sup>41</sup> S. Glasstone, *ibid.*, 1921, **119**, 1914.

form or the metastable yellow rhombic bipyramidal form; and these forms differ in density, in solubility, and in *E.M.F.* against lead in normal caustic soda.<sup>42</sup> There is some evidence that these forms are enantiotropic; but this point is in doubt, and further investigation is required to establish their relationship. Further physical investigation of the oxides of lead confirms the view of red lead as plumbous orthoplumbate and indicates the probable existence of a higher oxide in electrolytically deposited lead dioxide.<sup>43</sup>

Examination of the X-ray spectra of rare-earth oxides has identified Urbain's celtium as the element of atomic number 72, intermediate between lutecium, 175, and tantalum, 181.5, and a member of this group.<sup>44</sup>

### Group V.

Formation of ammonia in good yield from hydrogen and excess of nitrogen in electron tubes occurs with applied electromotive forces equal to or greater than the ionisation potential of nitrogen; <sup>45</sup> which is held to show that ionisation of nitrogen is the first step in this synthesis.

Decomposition of ammonium nitrate proceeds normally at 210–260°, yielding 98 per cent. nitrous oxide, but the presence of even 0.1 per cent. of ammonium or sodium chloride, or the over-heating of the pure nitrate, gives impure gas containing 30–50 per cent. of nitrogen; with the pure salt, the subsidiary reactions are probably  $\text{NH}_4\text{NO}_3 \rightleftharpoons \text{NH}_3 + \text{HNO}_3$  and  $5\text{NH}_3 + 3\text{HNO}_3 \longrightarrow 9\text{H}_2\text{O} + \text{N}_2$ , and the explosive decomposition at 300° may be represented as  $8\text{NH}_4\text{NO}_3 \longrightarrow 16\text{H}_2\text{O} + 2\text{NO}_2 + 4\text{NO} + 5\text{N}_2$ .<sup>46</sup> Ammonium chlorate is perfectly stable in cold saturated aqueous solutions, but if solid salt is present progressive decomposition occurs which finally becomes explosive; the solid decomposes, rapidly if enclosed, slowly if exposed, the residue being ammonium nitrate free from chloride. These phenomena are due to autoxidation, catalysed by the products of decomposition.<sup>47</sup>

A simple method has been described for the preparation of crystalline hydroxylamine by interaction of equivalent quantities of the hydrochloride and sodium ethoxide in absolute alcohol;

<sup>42</sup> M. P. Applebey and R. D. Reid, *T.*, 1922, **121**, 2129; see also F. M. Jaeger and H. C. Germs, *Z. anorg. Chem.*, 1921, **119**, 145; *A.*, ii, 65.

<sup>43</sup> S. Glasstone, *T.*, 1922, **121**, 58, 1456, 1469, 2091.

<sup>44</sup> A. Dauvillier, *Compt. rend.*, 1922, **174**, 1347; *A.*, ii, 463; G. Urbain, *ibid.*, 1349; *A.*, ii, 505.

<sup>45</sup> E. B. Andersen, *Z. Physik*, 1922, **10**, 54; E. Hiedmann, *Chem. Ztg.*, 1921, **45**, 1073; *A.*, ii, 562; *A.*, 1921, ii, 694.

<sup>46</sup> H. L. Saunders, *T.*, 1922, **121**, 698.

<sup>47</sup> F. Fairbrother, *J. Amer. Chem. Soc.*, 1922, **44**, 2419; *A.*, 1923, ii, 27.

the product differs from the purest hydroxylamine hitherto obtained only in being rather less stable.<sup>48</sup>

The mechanism of absorption of oxides of nitrogen by alkali is still in doubt; further evidence supports the view that oxidation of nitric oxide to nitrogen tetroxide proceeds without intermediate formation of nitrous anhydride; yet the absorption of a gaseous system NO-NO<sub>2</sub> by alkali hydroxide proceeds in a manner which can best be explained by assuming the presence of nitrous anhydride in small concentrations.<sup>49</sup> The fact that nitrogen pentoxide has unusual stability in presence of traces of ozone<sup>50</sup> is best explained by the assumption that its decomposition is catalysed by the products (which are reconverted immediately to pentoxide by ozone), as has been shown to be the case in the photochemical decomposition of nitrogen pentoxide and in the thermal decomposition of its solutions in carbon tetrachloride and chloroform.<sup>51</sup>

Evidence of the existence of an active form of hypophosphorous acid is again obtained from a study of its rate of reaction with cupric chloride; but any purely physical explanation<sup>52</sup> is rejected in favour of the idea that there may exist an equilibrium between the ordinary acid and its tervalent form, HP(OH)<sub>2</sub>, which would be expected to be very reactive.<sup>53</sup>

Two interesting methods are described for the purification of phosphoric oxide, hitherto a very tedious and wasteful operation, very necessary in precise work, but often omitted. In one the oxide is dropped into a rapid current of oxygen in an iron tube at 600—700°, the sublimate being condensed in a long wide glass continuation tube; 50 grams of pure oxide can thus be prepared from 100 grams of crude material in an hour.<sup>54</sup> The second method is ingenious and very simple: commercial phosphoric oxide is heated at 175—220° in ozonised air until fully oxidised: the product still contains, of course, any non-volatile impurity originally present, but it is free from lower oxides and is no more liable than the resublimed oxide to yield gas in high vacua. Evidence was obtained that the phosphorous oxide present in commercial phosphoric oxide reacts

<sup>48</sup> H. Lecher and J. Hofmann, *Der.*, 1922, 55, [B], 912; *A.*, ii, 442.

<sup>49</sup> E. Briner, S. Niewiazski, and J. Wiswald, *Helv. Chim. Acta*, 1922, 5, 432; *A.*, ii, 563; F. Foerster, *Ber.*, 1922, 55, [B], 490; *A.*, ii, 284; A. Sanfourche, *Compt. rend.*, 1922, 175, 460; *A.*, ii, 762.

<sup>50</sup> F. Daniels, O. R. Wulf, and S. Karrer, *J. Amer. Chem. Soc.*, 1922, 44, 2402; *A.*, 1923, ii, 24.

<sup>51</sup> Daniels and Johnston, *ibid.*, 1921, 43, 53; R. H. Lueck, *ibid.*, 1922, 44, 757; *A.*, ii, 433.

<sup>52</sup> *Ann. Reports*, 1921, 18, 41.

<sup>53</sup> A. D. Mitchell, *T.*, 1922, 121, 1624.

<sup>54</sup> G. I. Finch and R. H. K. Peto, *ibid.*, 692.

with water to form phosphine which, under the influence of electrical discharges (for example, produced by friction between mercury and glass), reacts with mercury to form the phosphide ( $\text{Hg}_3\text{P}_2$ ?) and hydrogen.<sup>55</sup>

Phosphine, with but little hydrogen, is best prepared by the action of 10 per cent. sulphuric acid on aluminium phosphide.<sup>56</sup>

A review of the past evidence and consideration of new experiments on the heat evolved by arsenic in cooling from various high temperatures confirm the transition point to yellow arsenic at about  $750^\circ$ , but indicates that whilst brown or "amorphous" arsenic may be, as has been supposed, a distinct monotropic modification, "grey" arsenic is probably not an allotropic form, but merely an intermediate stage in the conversion of colloidal arsenic to the crystalline state.<sup>57</sup> This is clearly a case in which X-ray analysis might give important information.

Arsenic combines with aluminium at  $750^\circ$  to give a brown, amorphous compound,  $\text{Al}_3\text{As}_2$ , infusible and undissociated at temperatures up to  $1600^\circ$ , but apparently dissociating at the ordinary temperature, as old specimens slowly deposit yellow arsenic and leave a residue of black arsenic on solution in hydrochloric acid, whereas the freshly prepared substance is completely soluble in acid.<sup>58</sup>

Bismuth subiodide,  $\text{BiI}_2$ , has been obtained in red, orthorhombic needles, which dissolve in aqueous potassium iodide to an orange solution, act as a strong reducing agent, and decompose to the tri-iodide and bismuth at  $400^\circ$ .<sup>59</sup>

It has been stated that tantalum pentachloride is a good conductor whilst columbium pentachloride is an insulator, but measurements with the anhydrous chlorides show that the conductivities are about the same and extremely small, about  $0.25 \times 10^{-6}$  mhos.<sup>60</sup>

#### Group VI.

Liquid ozone and oxygen are only partly miscible, and are readily separated by fractional distillation. Pure ozone so obtained has been employed for a redetermination of physical constants (m. p. —  $249.7^\circ$ ; b. p. —  $112.4^\circ$ ;  $T_k$  —  $5^\circ$ ;  $P_k$  64.8 atm.;  $d_{-182}^{182}$  1.71),<sup>61</sup> and for an ingenious and skilful determination of vapour density

<sup>55</sup> J. J. Manley, *T.*, 1922, **121**, 331.

<sup>56</sup> L. Moser and A. Brukl, *Z. anorg. Chem.*, 1921, **121**, 73; *A.*, ii, 393.

<sup>57</sup> P. N. Laschtschenko, *T.*, 1922, **121**, 972.

<sup>58</sup> Q. A. Mansuri, *ibid.*, 2272.

<sup>59</sup> H. G. Denham, *J. Amer. Chem. Soc.*, 1921, **43**, 2367; *A.*, ii, 218.

<sup>60</sup> W. Biltz and A. Voigt, *Z. anorg. Chem.*, 1921, **120**, 71; *A.*, ii, 302.

<sup>61</sup> E. H. Riesenfeld and G. M. Schwab, *Ber.*, 1922, **55**, [B], 2088; *A.*, ii, 637; *Z. Physik*, 1922, **11**, 12; *A.*, ii, 761.

by direct weighing of a bulb filled with ozone, the pressure at the time of filling being extrapolated from the observed growth of pressure in the bulb after weighing. The molecular weight found confirms the formula  $O_3$ ,<sup>62</sup> and neither investigation affords any evidence whatever of the existence of higher polymerides of oxygen.

Ozone oxidises nitrogen tetroxide instantly to the pentoxide, the completion of the quantitative reaction  $N_2O_4 + O_3 \rightarrow N_2O_5 + O_2$  being sharply indicated by disappearance of colour, so that a true *titration* can thus be performed in the gaseous phase.<sup>63</sup>

Sulphur dioxide partly oxidises cuprous chloride in concentrated hydrochloric acid according to the equation (i)  $2Cu_2Cl_2 + SO_2 + 4HCl \rightleftharpoons 4CuCl_2 + 2H_2O + S$ ; but the reverse change is obscured by a secondary action, (ii)  $6CuCl_2 + S + 4H_2O \rightarrow 3Cu_2Cl_2 + 6HCl + H_2SO_4$ . With increasing acid concentration, first cuprous sulphide, then mixtures of the sulphide and sulphur, and finally sulphur only are precipitated. A reaction analogous to (i) occurs with mercurous chloride in hydrochloric acid concentrations from 8*N* to 2*N*, whilst further reduction occurs (*a*) to mercurous chloride and mercury at 2*N* — 0.16*N*, and (*b*) to mercury only at acid concentrations less than 0.02*N*.<sup>64</sup>

Sodium sulphite or bisulphite, dropped into warm dilute aqueous sulphuric acid, yields hydrogen sulphide, probably by the reaction  $4H_2SO_3 \rightarrow H_2S + 3H_2SO_4$ , which may well be an intermediate stage in the known reaction  $3H_2SO_3 \rightarrow 2H_2SO_4 + H_2O + S$ ; <sup>65</sup> and there is evidence that hydrated sodium sulphite, excluded from air, undergoes autoxidation to sulphate.<sup>66</sup>

Freshly prepared solutions of bisulphites show an absorption band characteristic of metabisulphites and therefore probably contain a small proportion of the latter in equilibrium; they are stable in light if oxygen is excluded, but in its presence are oxidised with formation of sulphate and develop an absorption band characteristic of hydrated sulphur dioxide.<sup>67</sup>

Measurements of viscosity, conductivity, and contraction on mixing show that a complex,  $H_2SO_4.H_2O.(C_2H_5)_2O$ , is present in systems of sulphuric acid, water, and ether.<sup>68</sup>

Aluminium selenide,  $Al_2Se_3$ , easily prepared from its elements

<sup>62</sup> S. Karrer and O. R. Wulf, *J. Amer. Chem. Soc.*, 1922, **44**, 2391.

<sup>63</sup> O. R. Wulf, F. Daniels, and S. Karrer, *ibid.*, 2398; *A.*, 1923, ii, 23.

<sup>64</sup> W. Wardlaw and F. W. Pinkard, *T.*, 1921, **121**, 210; L. M. Stewart and W. Wardlaw, *ibid.*, 1481.

<sup>65</sup> G. M. Bennett, *ibid.*, 1922, **121**, 1794.

<sup>66</sup> S. L. Shenofield, F. C. Vilbrandt, and J. R. Withrow, *Chem. and Met. Eng.*, 1921, **25**, 953; *A.*, ii, 45.

<sup>67</sup> E. C. C. Baly and R. A. Bailey, *T.*, 1922, **121**, 1813.

<sup>68</sup> J. R. Pound, *ibid.*, 941.



as a light brown powder, unstable in air, affords, by reaction with acids, a convenient source of hydrogen selenide, which can be purified by liquefaction at  $-80^{\circ}$  and re-evaporation. The dry gas is stable in ordinary daylight and unaffected by dry oxygen.<sup>69</sup> Hydrogen telluride has been prepared in a similar way and resembles the selenide except in its lesser stability to light and oxidation.<sup>70</sup> Further work is recorded on the properties of selenium oxychloride,<sup>71</sup> and the oxybromide has been obtained, by the action of bromine on a mixture of selenium and selenium dioxide at  $0^{\circ}$ , as a reddish-yellow solid, m. p.  $41.5^{\circ}$ , b. p.  $217^{\circ}/740$  mm. with much decomposition,  $d_{40}^{20} 3.38$ , which generally resembles the oxychloride in its remarkable chemical activity.<sup>72</sup>

A convenient method is described for the preparation of selenium dioxide by combustion of selenium in oxygen containing nitrous fumes;<sup>73</sup> and it has been shown that it forms only one hydrate,  $\text{SeO}_2 \cdot \text{H}_2\text{O}$ .<sup>74</sup> Nitrosylselenic acid,  $\text{NO} \cdot \text{O} \cdot \text{SeO}_2 \cdot \text{OH}$ , obtained by the action of liquid nitrogen trioxide on anhydrous selenic acid, is a colourless, crystalline solid melting at  $80^{\circ}$  with decomposition and unstable even at the ordinary temperature.<sup>75</sup>

Tellurium, purified by distillation and crystallised by solidification or sublimation, has  $d 6.310$ , which is unchanged by long heating at various temperatures. It is probable, therefore, that tellurium does not exhibit the dynamic allotropy which has been attributed to it.<sup>76</sup> Oxidation of tellurium tetrachloride with chlorine is a convenient method of obtaining pure telluric acid in almost theoretical yield.<sup>77</sup>

A study of the solubility of chromium trioxide in sulphuric acid<sup>78</sup> shows that when the concentration of the latter is 85—95 per cent. the solid phase is brown, minutely crystalline  $\text{CrO}_3 \cdot \text{SO}_3$ ; whilst in stronger acid the solid phase is probably the chromisulphuric acid,  $\text{CrO}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ , described by Gay-Lussac and recently prepared, together with the corresponding chromiselenic acid and certain salts of these acids.<sup>79</sup>

<sup>69</sup> L. Moser and E. Doctor, *Z. anorg. Chem.*, 1921, **118**, 284; *A.*, ii, 46.

<sup>70</sup> L. Moser and K. Ertl, *ibid.*, 269; *A.*, ii, 48.

<sup>71</sup> V. Lenher, *J. Amer. Chem. Soc.*, 1922, **44**, 1664; *A.*, ii, 706; compare *Ann. Reports*, 1921, **18**, 53.

<sup>72</sup> *Idem.*, *ibid.*, 1668; *A.*, ii, 707.

<sup>73</sup> J. Meyer, *Ber.*, 1922, **55**, [B], 2082; *A.*, ii, 639.

<sup>74</sup> W. Manchot and K. Ortner, *Z. anorg. Chem.*, 1922, **120**, 300; *A.*, ii, 283.

<sup>75</sup> J. Meyer and W. Wagner, *Ber.*, 1922, **55**, [B], 690; *A.*, ii, 372.

<sup>76</sup> A. Damiens, *Compt. rend.*, 1922, **174**, 1344, 1548; *A.*, ii, 498, 562.

<sup>77</sup> J. Meyer and H. Moldenhauer, *Z. anorg. Chem.*, 1921, **119**, 132; *A.*, ii, 49.

<sup>78</sup> L. F. Gilbert, H. Buckley, and I. Masson, *T.*, 1922, **121**, 1934.

<sup>79</sup> J. Meyer and V. Stateczny, *Z. anorg. Chem.*, 1922, **122**, 1; *A.*, ii, 773.

The dichlorides of molybdenum, tungsten, and tantalum have been prepared, in some cases by new methods, and have been shown uniformly to be represented by the formula  $\text{HM}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$  and not by the complex formulæ hitherto given to them.<sup>80</sup>

Metallic tungsten acts slowly on thoria at  $2400^\circ$  in a vacuum and in argon, nitrogen, or hydrogen to form thorium and tungsten trioxide, the latter appearing in part to react with tungsten to form a grey, metallic, crystalline substance, very stable to acids and alkalis, which may be a "bronze" of the type  $\text{Th}(\text{WO}_3)_n$ , where  $n = 3 - 10$ .<sup>81</sup>

The green colour sometimes observed in tungsten trioxide is due to surface reduction to lower oxides,<sup>82</sup> and X-ray examination of the hydrated oxides shows the existence of  $\text{H}_2\text{WO}_4$  and  $\text{H}_4\text{WO}_5$  as distinct compounds,<sup>83</sup> the former being confirmed also by the form of the vapour pressure-composition curve.<sup>84</sup> Evidence has been obtained that the sodium tungstate,  $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$ , is really an acid salt,  $4(\text{Na}_2\text{WO}_4) \cdot 6(\text{H}_2\text{WO}_4) \cdot 17\text{H}_2\text{O}$ , and corresponding salts of other bases, differing, however, in water content, have been isolated.<sup>85</sup>

An icositetrahydrate of uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , is found to exist at temperatures below  $-20^\circ$ .<sup>86</sup>

### Group VIII.

The photography of the spectrum of fluorine, excited by the discharge between gold electrodes, deserves mention because of the attendant experimental difficulties.<sup>87</sup> A simple method for the preparation of pure ammonium hydrogen fluoride consists in treating aqueous hydrofluosilicic acid with excess of ammonia, filtering, concentrating in platinum, and subliming the product.<sup>88</sup>

The existence of  $\text{HClBr}_2$ , deduced by Berthelot from the heat of solution of bromine in hydrochloric acid, is confirmed and that of  $\text{HClI}_2$  and  $\text{HBrI}_2$  evidenced by measurements of the distribution of free halogen between aqueous halogen acids and an immiscible solvent.<sup>89</sup>

The normal chlorites of sodium, lithium, calcium, strontium,

<sup>80</sup> K. Lindner *et al.*, *Ber.*, 1922, **55**, [B], 1458; *A.*, ii, 509.

<sup>81</sup> C. J. Smithells, *T.*, 1922, **121**, 2236; compare E. Wedekind, *Edel-Erden und -Erze*, 1922, **3**, 109.

<sup>82</sup> J. A. M. van Liempt, *Z. anorg. Chem.*, 1921, **119**, 310; *A.*, ii, 73.

<sup>83</sup> H. C. Burger, *ibid.*, 1922, **121**, 240; *A.*, ii, 508.

<sup>84</sup> G. F. Hüttig and B. Kurre, *ibid.*, 1922, **122**, 44; *A.*, ii, 773.

<sup>85</sup> E. F. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2027; *A.*, ii, 774.

<sup>86</sup> F. E. E. Germann, *ibid.*, 1466; *A.*, ii, 649.

<sup>87</sup> W. R. Smythe, *Astrophys. J.*, 1921, **54**, 133; *A.*, ii, 99.

<sup>88</sup> M. Ikawa, *J. Chem. Soc. Japan*, 1921, **42**, 768.

<sup>89</sup> P. Rây and P. V. Sarkar, *T.*, 1922, **121**, 1449.

and univalent thallium have been prepared and are found to be unstable substances, exploding when dry by percussion and decomposed by heat, in the case of the sodium salt according to the equation  $3\text{NaClO}_2 \longrightarrow 2\text{NaClO}_3 + \text{NaCl}$ .<sup>90</sup>

An examination of the mineral fluorite by means of the X-ray spectrograph has given indications<sup>91</sup> that it may contain the element of atomic number 61, a member of this group.

### Group VIII.

The amount of electrolytic iron foil dissolved by aqueous sulphuric acid (in thirty-four hours at 15°) has been found to vary with acid concentration in a remarkable manner, rising steadily with 0.5*N*- to 2*N*-acid, then falling with 3*N*-acid, and again increasing to progressively higher values with 4*N*- and 5*N*-acid. Another series of experiments shows that when a disk of pure iron is rotated for thirty minutes in acids of concentrations *N*/5, *N*/10, *N*/50, and *N*/100, the amount of iron dissolved depends only on the velocity of rotation, with which it increases linearly up to a peripheral speed of 35 m.p.h., in marked contrast to the corrosion of iron in aerated water, which ceases at a speed of 5 m.p.h.<sup>92</sup>

Samples of ferric oxide prepared by twenty-seven different methods have been found to give identical X-ray spectra, which affords strong evidence that, despite their outward differences, they are really the same form of the compound.<sup>93</sup> A peculiar iron salt,  $\text{FeSO}_4\text{Cl}\cdot 6\text{H}_2\text{O}$ , has been obtained by treating a concentrated solution of ferrous sulphate with chlorine, and by other methods.<sup>94</sup>

It is satisfactory to record the publication of a study of the general equilibrium in the system  $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$  from 50—200° which resolves in a convincing fashion the doubt and complexity associated with the hydrates and sulphates of ferric oxide. The components in suitable proportions were heated together in sealed tubes for times so prolonged as to ensure the attainment of equilibrium (its non-attainment being the probable cause of uncertain and conflicting results in many previous investigations of the system), and the liquid and wet solids were separated and analysed. Determination of the composition of the dry solid phase was effected by Schreinemakers's "residue" method, controlled by microscopic observations, especially of refractive index and dispersion. The results, embodied

<sup>90</sup> G. R. Levi, *Gazzetta*, 1922, **52**, i, 417; *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 212, 370; *A.*, ii, 567.

<sup>91</sup> A. Hadding, *Z. anorg. Chem.*, 1922, **122**, 195; *A.*, ii, 780.

<sup>92</sup> J. A. Newton Friend and J. H. Dennett, *T.*, 1922, **121**, 41.

<sup>93</sup> J. A. Hedvall, *Z. anorg. Chem.*, 1922, **120**, 327; **121**, 217; *A.*, ii, 300, 381.

<sup>94</sup> O. Röhm, *Collegium*, 1921, No. **614**, 282; *A.*, ii, 648.

in a series of triangular diagrams and a solid model, indicate that the only solid phases existing within the range studied are :<sup>95</sup>  $\text{Fe}_2\text{O}_3$ ;  $\text{Fe}_2\text{O}_3, \text{H}_2\text{O}$ ;  $3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 9\text{H}_2\text{O}$ ;  $\text{Fe}_2\text{O}_3, 2\text{SO}_3, \text{H}_2\text{O}$ ;  $\text{Fe}_2\text{O}_3, 2\text{SO}_3, 5\text{H}_2\text{O}$ ;  $2\text{Fe}_2\text{O}_3, 5\text{SO}_3, 17\text{H}_2\text{O}$ ;  $\text{Fe}_2\text{O}_3, 3\text{SO}_3$  (two forms: rhombohedral and orthorhombic);  $\text{Fe}_2\text{O}_3, 3\text{SO}_3, 6\text{H}_2\text{O}$ ;  $\text{Fe}_2\text{O}_3, 3\text{SO}_3, 7\text{H}_2\text{O}$ ;  $\text{Fe}_2\text{O}_3, 4\text{SO}_3, 3\text{H}_2\text{O}$ ;  $\text{Fe}_2\text{O}_3, 4\text{SO}_3, 9\text{H}_2\text{O}$ . Other investigations confirm the existence, as phases stable in part of the system at  $18^\circ$  and  $25^\circ$ , of  $\text{Fe}_2\text{O}_3, 3\text{SO}_3, 7\text{H}_2\text{O}$  and  $\text{Fe}_2\text{O}_3, 4\text{SO}_3, 9\text{H}_2\text{O}$ .<sup>96</sup> The colourless form of iron alum occasionally encountered is shown to be due to the presence of ferric hydroxide as an impurity.<sup>97</sup>

In the course of further studies on the properties of subsidiary valency groups, the trihydrate and tri- and hexa-ammines of cobaltous fluoride have been prepared.<sup>98</sup>

Aqueous solutions of ruthenium tetroxide conduct electricity, have a weak acid reaction, and form salts with alkalis; but of these only the ammonium salt,  $(\text{NH}_4)_2\text{RuO}_5$ , could be obtained in a pure state.<sup>99</sup>

<sup>95</sup> E. Posnjak and H. E. Merwin, *J. Amer. Chem. Soc.*, 1922, **44**, 1965; *A.*, ii, 772.

<sup>96</sup> M. P. Appleby and S. H. Wilkes, *T.*, 1922, **121**, 337.

<sup>97</sup> J. Bonnell and E. P. Perman, *T.*, 1921, **119**, 1994.

<sup>98</sup> G. L. Clark and H. K. Buckner, *J. Amer. Chem. Soc.*, 1922, **44**, 230; *A.*, ii, 300.

<sup>99</sup> F. Krauss, *Z. anorg. Chem.*, 1921, **119**, 217; *A.*, ii, 75.

H. V. A. BRISCOE.

## ORGANIC CHEMISTRY.

### PART I.—ALIPHATIC DIVISION.

THE general arrangement of the aliphatic compounds which was adopted in previous Reports has been followed in the present case, and, whilst the headings of the different sections indicate broadly the character of the compounds considered in the various groups, an arbitrary choice has sometimes to be made. Theoretical discussions based on an extended survey of reactions obviously present this difficulty to the Reporter, and it is imperative that generalisations such as those which have appeared on the induced polarity of atoms, and the interpretation of the theory of partial valencies on an electronic basis, by Lapworth and by Kermack and R. Robinson,<sup>1</sup> should not be relegated to any single sub-section of compounds. These authors have now reviewed their generalisations in the light of the Thomson and Lewis-Langmuir theory of the atom and of valency, and this may be regarded as a physical basis for their hypotheses. Whilst it is impossible in a sectional report to do justice to these theoretical considerations inasmuch as they cover the whole field of reactions in organic chemistry, nevertheless occasional references will be found in the succeeding pages.

#### *Hydrocarbons.*

A notable feature of the recent researches on hydrocarbons is the tendency to focus on the study of the additive reactions of the simpler unsaturated members of the group. Attention has been directed to the conditions governing the hydrogenation<sup>2</sup> of ethylene and acetylene in the presence of nickel or of nickel-mercury catalysts. With the latter, acetylene may be reduced at 25—35° to both a light oil consisting of ethylenic hydrocarbons and a heavier oil. In the preparation of either ethane or ethylene from acetylene, it is advantageous to dilute the acetylene with the expected products. Combination of anhydrous sulphuric acid with acetylene occurs under pressure at 0° in presence of mercuric

<sup>1</sup> *T.*, 1922, 121, 416, 427.

<sup>2</sup> E. K. Rideal, *T.*, 1922, 121, 309; K. Oda, *J. Chem. Ind. Japan*, 1921, 24, 1161; *A.*, 1921, i, 841.

sulphate<sup>3</sup> with the almost quantitative formation of vinylsulphuric acid,  $\text{CH}_2\text{:CH}\cdot\text{SO}_3\cdot\text{OH}$ . Acetonitrile is produced at higher temperatures by combination of acetylene with ammonia, but, in presence of excess of the former, pyrrole and picoline are among the products. Similar evidence of polymerisation of a hydrocarbon during its combination with other reagents is furnished in the case of ethylene, which, under the influence of the silent discharge, unites with nitrogen to give a complex nitrile,  $\text{C}_{18}\text{H}_{31}\cdot\text{CN}$ .

The catalytic method for the dehydration of alcohols has been applied in a preparation of pure propylene, the physical constants of which have now been determined with accuracy.<sup>4</sup> It is of interest that this gaseous hydrocarbon is formed by isomeric change from cyclopropane at 600—700°; the reversible reaction,  $\text{cyclopropane} \rightleftharpoons \text{propylene}$ , is thus an example of the three-carbon tautomerism which has been studied by Thorpe and his school. Consideration of the kinetics of open-chain compounds and thermochemical data accord with the view that the Baeyer strain theory as applied to double linkings is open to criticism, since it is known that an ethylenic bond is more easily formed than a five-membered ring.<sup>5</sup> Quite different in character is the reaction which leads, under similar conditions to the above, from ethylene to butadiene,<sup>6</sup> in which case a synthetic operation is involved with loss of hydrogen. The hydrocarbon synthesised from pinacolin by the application of the Grignard reagent followed by dehydration has the formula  $\text{CMe}_3\cdot\text{CMe}\cdot\text{CH}_2$ , which undergoes reduction by Paal's method to a new heptane, trimethylisopropylmethane.<sup>7</sup> When pinacolin is chlorinated by phosphorus pentachloride, the normal dichloride is produced along with the unsaturated derivative,  $\text{CMe}_3\cdot\text{CCl}\cdot\text{CH}_2$ . Elimination of hydrogen chloride leads to a dimethylbutinene which on reduction gives rise to  $\beta\beta$ -dimethylbutane. Physical constants of these hydrocarbons have been determined.

Separation of two geometric isomerides by fractional distillation is a simple procedure in the case of maleic and fumaric acids, but it would appear difficult of achievement with hydrocarbons. Success has, however, been attained in the separation of the two

<sup>3</sup> Brit. Pat. 156121 and 147067; *A.*, i, 517; *A.*, 1921, i, 852; Miyamoto, *J. Chem. Soc. Japan*, 1922, 43, 21; *A.*, i, 418.

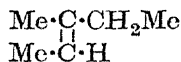
<sup>4</sup> M. Trautz and K. Winkler, *J. pr. Chem.*, 1922, [iii], 104, 44, 53; *A.*, i, 909, 926.

<sup>5</sup> J. P. Wibaut, *Rec. trav. chim.*, 1922, 41, 441; *A.*, i, 909; Wojnicz Sianozencki, *Rozniki Chemji*, 1921, 1, 244; *A.*, i, 330.

<sup>6</sup> Zanetti, Suydam, and Offner, *J. Amer. Chem. Soc.*, 1922, 44, 2036; *A.*, i, 977.

<sup>7</sup> Chavanne and Lejeune, *Bull. Soc. Chim. Belg.*, 1922, 31, 98; *A.*, i, 417; Risseghem, *ibid.*, 62; *A.*, i, 313.

$\gamma$ -methyl- $\Delta^7$ -pentenes obtained from methyldiethylcarbinol by dehydration with *p*-toluenesulphonic acid : <sup>8</sup>



Their boiling points differ by less than 5°, and the refractive indices are distinctive. Both yield methyl ethyl ketone on oxidation, and combine additively with bromine, but hydrochloric acid effects isomerisation of one of the stereoisomerides.

Grignard reactions have been applied in improvements of recognised methods of preparing alkyl derivatives of cadmium and mercury, whilst recent investigations with metallic carbides <sup>9</sup> provide not only a simplified procedure for obtaining methane, but show that with superheated steam liquid products containing 60 per cent. of benzene may be collected, and by conducting the process under appropriate pressures terpenes and higher polymerised hydrocarbons are formed. On the analogy of the Würtz reaction, the anticipated result of bringing together methylene iodide and aluminium in anhydrous ether is the formation of ethylene. This conclusion is in need of verification in view of the contradictory observations of two independent workers; <sup>10</sup> but it seems clear that in any case the formation of ethylene or some analogue is only a secondary reaction. The chief product either from methylene bromide or iodide appears to be an interesting unsaturated type of organometallic halide, namely,  $\text{CH}_2\text{:AlX}$ , which is decomposed by water or alcohol to give methane. It combines additively with iodine, yielding a saturated compound, which also reacts with water to give methyl iodide.

Investigation of all the simpler unsaturated hydrocarbons with a view to their easy recognition is a necessary preliminary to the systematic survey of the depolymerised products of caoutchouc, and this inquiry may well run parallel with a serious study of the important phenomenon of polymerisation which, not alone in the hydrocarbon series, but also in the carbohydrate group, is a vital factor governing the constitution of the more complex natural products.

Polymerisation of vinyl chloride in ether or alcohol is promoted by extreme ultra-violet light at the ordinary temperature, and metallic salts, especially those of uranium, catalyse the reaction in sunlight. The product is a white powder which separates from

<sup>8</sup> Risseghem, *Bull. Soc. Chim. Belg.*, 1922, **31**, 213; *A.*, i, 909.

<sup>9</sup> O. Ohmann, *Z. physikal. Chem. Unterr.* 1921, **34**, 76; *A.*, i, 2; Plauson and v. Tischenko, *Chem. Zentr.*, 1922, ii, 442; *A.*, i, 818.

<sup>10</sup> Failliebin, *Compt. rend.*, 1922, **174**, 112; *A.*, i, 119; V. Thomas, *ibid.*, 464; *A.*, i, 330.

solvents as an elastic film.<sup>11</sup> Hydrogenation of caoutchouc in presence of platinum leads to a product  $(C_5H_{10})_x$  which remains a colloid and apparently is not depolymerised. Distillation of this product in a high vacuum yields degraded products which are simple unsaturated hydrocarbons. The results favour the theory that the caoutchouc molecule is composed of isoprene polymerised in chains of such length as to minimise their unsaturated character. The views of Harries are contested on several grounds.

Thiele's theory of the mode of attachment of addenda to a conjugated unsaturated system such as that of isoprene is supported by Staudinger and his co-workers, who have shown that both with hydrogen bromide and bromine combination occurs in the  $\alpha$ - and  $\delta$ -positions. Whether this is so under all conditions remains in doubt, since contradictory evidence is furnished by A. G. Bergmann.<sup>12</sup>

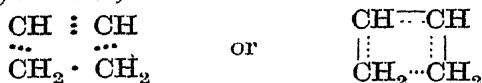
In the communication by Kermack and Robinson referred to in the introduction the theory of partial valencies and the attachment of addenda is interpreted on the basis of the Lewis-Langmuir hypothesis and it is shown that the usual expressions,



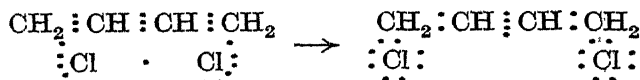
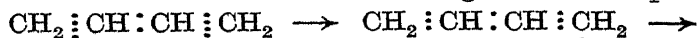
become (if it is assumed on the physical basis that the symbols  $\equiv$ ,  $\equiv\equiv$ ,  $\equiv\equiv\equiv$ ,  $\equiv\equiv\equiv\equiv$ , imply electrons to the number of four, three, two, and one, respectively, held in common by two atoms) the following :



The latter represents an extreme and unstable condition of the former non-polarised molecule, and another more stable form would be the cyclic one, such as :



The system may be an oscillating one in which the terminal carbon atoms become in turn feebly electropositive and electronegative, the reagents taking advantage of these momentary manifestations of polarity; the process of addition is represented by an interchange of electrons of which the following is one example :



<sup>11</sup> J. Plotnikow, *Z. wiss. Photochem.*, 1922, **21**, 117; *A.*, i, 419; H. Staudinger and J. Frittschi, *Helv. Chim. Acta*, 1922, **5**, 785; *A.*, i, 1043.

<sup>12</sup> *Helv. Chim. Acta*, 1922, 5, 743; *A.*, i, 978; *J. Russ. Phys. Chem. Soc.*, 1920, 52, 24; *A.*, i, 1106.



It is recognised, however, that other phases of interchange must be provided for to admit of alternative modes of addition under conditions such as those which lead either to trimethylene dibromide or propylene dibromide by the union of hydrogen bromide and allyl bromide, and these manifestations of "secondary conjugation" are dealt with. With a substituted system such as that which occurs in muconic acid, the attachment of hydrogen follows the Thiele rule, but bromine, on the contrary, combines in the  $\alpha$ - and  $\beta$ -positions, and it is suggested<sup>13</sup> that the rule has been too hastily accepted as a generalisation on evidence which is restricted. It is contended that the Thiele rule should be confined to those cases of conjugation in which X and X' in the formula  $XCH=CH-CH=CHX'$  are both fully saturated residues.

Experiments with petroleum reveal the disconcerting fact that polymerisation may accompany the formation of ozonides, and such considerations may have to be taken into account in evaluating the results of constitutional work undertaken with the use of ozone.<sup>14</sup> A study of the constituents of paraffin wax has given promising data pointing to the possibility of effecting separation of the individual hydrocarbons, but as the research is incomplete a discussion of the results may for the present be held over. The same may be said also of several investigations in which the higher paraffins have been submitted to catalytic oxidation with air or oxygen. The problem is complicated by the tendency of the normal fatty acids to undergo further oxidation to dibasic and hydroxy-acids, so that the isolation of palmitic and stearic acids may be prevented unless means can be devised to fix these primary products in such a way as to resist this tendency.

#### *Alcohols and Derivatives.*

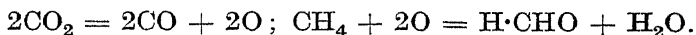
Synthetic methods for the manufacture of methyl alcohol and formaldehyde excite the interest of all chemists, inasmuch as the demand on these raw materials extends to both pure and applied chemistry. As the two substances are so intimately related in origin, it is inadvisable to separate the reviews of several processes which claim to have achieved success in the synthesis of both or either of the products. Selection of the initial materials for the purpose must obviously depend on economic factors, and the utilisation of carbon monoxide and hydrogen is reported in two of the methods, whilst, in a third, carbon dioxide and methane are employed. The Badische process<sup>15</sup> is based on the conversion

<sup>13</sup> J. P. C. Chandrasena and C. K. Ingold, *T.*, 1922, **121**, 1306.

<sup>14</sup> R. Koetschau, *Z. angew. Chem.*, 1922, **35**, 509; *A.*, i, 977.

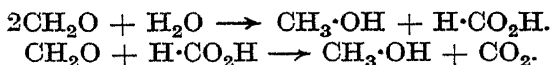
<sup>15</sup> Brit. Pat. 173097; *A.*, i, 218.

of lithium carbonate into formate by the agency of carbon monoxide and water under pressure and at a temperature above 120°. The lithium formate is afterwards decomposed at about 400° in a current of moist hydrogen with the production of methyl alcohol and ketones, and the by-product in the first reaction is carbon dioxide. In another process,<sup>16</sup> purified "suction gas" or water-gas is passed rapidly over catalysts containing nickel, copper, and aluminium at 300—400° under 10 atmospheres, when it is transformed into formaldehyde and methane. Conversely, the oxidation of the latter hydrocarbon forms the basis of a third process<sup>17</sup> yielding both methyl alcohol and formaldehyde. By oxidation of methane at 500—700° with carbon dioxide in constricted tubes made of nickel, copper, or silver, the following reactions occur :



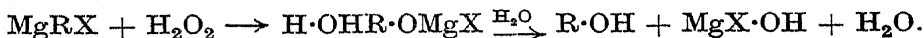
The yield of methyl alcohol is favoured by a slow passage of the mixed gases through the tubes and by introducing hydrogen into the mixture. With rapid flow of gases, however, the yield of formaldehyde amounts to 56 per cent. of the methane employed. E. W. Blair and T. S. Wheeler<sup>18</sup> have reinvestigated the production of formaldehyde by the circulation of mixtures of ethylene and oxygen over catalysts. By varying the conditions and the proportions of the mixture they were able to increase the yield of formaldehyde to 75 per cent.

Alcoholic fermentation of formaldehyde solutions is effected by osmium, and methyl alcohol and carbon dioxide are produced in the ratio of two to one, a reaction which seems to be capable of the following formulation :<sup>19</sup>



The activity of the osmium diminishes, however, rather rapidly.

Simple alcohols such as those of *isobutyl* and *isoamyl* may be prepared from the appropriate Grignard reagents<sup>20</sup> by the agency of hydrogen peroxide, and good yields are obtained. The character of the initial additive compounds suggests the representation of hydrogen peroxide by the formula  $\text{O}:\text{OH}\cdot\text{H}$  at the moment of its participation in the reaction :



<sup>16</sup> E. J. Lush, Brit. Pat. 180016; *A.*, i, 625.

<sup>17</sup> O. Traun, Brit. Pat. 156148; *A.*, i, 522.

<sup>18</sup> *J. Soc. Chem. Ind.*, 1922, **41**, 303T; *A.*, i, 917.

<sup>19</sup> E. Müller, *Ber.*, 1921, **54**, [B], 3214; *A.*, i, 110; H. Müller, *Helv. Chim. Acta*, 1922, **5**, 627; *A.*, i, 809.

<sup>20</sup> B. Oddo and R. Binaghi, *Gazzetta*, 1921, **51**, ii, 343; *A.*, i, 314.

Whilst Grignard reactions involving the use of ketones and esters usually give rise to tertiary alcohols, yet the  $\alpha$ -disubstituted ketones and esters lead to the formation of secondary alcohols, provided that the alkyl group in the Grignard reagent has a normal chain and contains not more than four carbon atoms.<sup>21</sup> Since excellent yields are claimed for the synthesis of secondary alcohols by this procedure, the method is doubtless a valuable one.

Acetylenic glycols of the general type  $\text{OH}\cdot\text{CRR}'\cdot\text{C}:\text{C}\cdot\text{CRR}'\cdot\text{OH}$  may be prepared by leading acetylene, under pressure, into the sodium derivatives of ketones, the latter sodium derivatives being easily formed by the aid of sodamide.<sup>22</sup> The conditions governing the formation of another unsaturated alcohol, namely, vinyl alcohol, have been studied by Evans and Looker, whilst a new synthesis of glycerol<sup>23</sup> from glycollaldehyde is effected by condensation with nitromethane, followed by reduction and treatment of the resulting aminoglycol with nitrous acid. In a similar way, glucose has been converted into crystalline  $\alpha$ -glucoheptol.

Of the available routes to the formation of the pure representatives of the chloro- and bromo-hydrins of glycerol, that which has been explored by J. Read and E. Hurst<sup>24</sup> is to be recommended. Allyl alcohol provides a suitable starting point, and it is shown that the hypohalogenous acids combine smoothly, yielding the monohalogenhydrins and also, as by-products, the dihalogenhydrins.

A novel and welcome variation of the usual reagents for the preparation of chlorohydrins from ethylenic hydrocarbons is provided by the recognition that monochlorocarbamide, obtained by chlorinating urea in aqueous solution, readily combines with olefines in presence of dilute acetic acid to give the corresponding chlorohydrins.<sup>25</sup> Several new chlorohydrins and their related ethylene oxide compounds have been obtained by this means, and, judging from the applications which have so far been studied, the reaction seems to be general. Ethylene oxide itself is of value in preparing by a direct method the chloroethyl esters of all types of acids.<sup>26</sup> This gaseous oxide combines additively with acid chlorides at their boiling point with immediate formation of esters in which the halogen is present in the alcohol residue. Another use to which chlorohydrins may be put is illustrated by the almost quantitative synthesis of ethylene cyanohydrin by means of sodium cyanide in cold aqueous solution.

<sup>21</sup> J. Leroide, *Ann. Chim.*, 1921, [ix], 16, 354; *A.*, i, 215.

<sup>22</sup> R. Locquin and S. Wouseng, *Compt. rend.*, 1922, 174, 1427; *A.*, i, 617.

<sup>23</sup> A. Pictet and A. Barbier, *Helv. Chim. Acta*, 1921, 4, 924; *A.*, i, 4.

<sup>24</sup> *T.*, 1922, 121, 989.

<sup>25</sup> A. Detœuf, *Bull. Soc. chim.*, 1922, [iv], 31, 102, 169, 176; *A.*, i, 236.

<sup>26</sup> J. Altwegg and J. Landrивon, U.S. Pat. 1393191; *A.*, i, 315.

The well-known phenomenon of the occurrence of hydrogen peroxide during the atmospheric oxidation of ether is now ascertained to be due to the formation of an ether peroxide<sup>27</sup> which is volatile and decomposes under the influence of light, but in presence of acidified water hydrogen peroxide is produced quantitatively.

### *Aldehydes and Ketones.*

In the foregoing section devoted to the alcohols and their derivatives, reference is made to developments in the synthetic production of formaldehyde and methyl alcohol. Numerous researches have been undertaken on problems involving the study of derivatives of formaldehyde, and some of these have an industrial application. An example is the preparation of a powerful reducing agent by suspending zinc dust in "formalin" solution and passing sulphur dioxide into the mixture through a Chamberland filter.<sup>28</sup> The zinc-formaldehyde hyposulphite which crystallises from solution is claimed to be more economical in use for the reduction of dyestuffs than the usual reagents. Distillation of formaldehyde in presence of sulphur dioxide gives rise to sulphiformin,  $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}\cdot\text{OH}$ , which has antiseptic and reducing properties and is easily decomposed into formic acid.<sup>29</sup> A similar transformation of formaldehyde into formic acid by the use of catalysts is described which resembles the Cannizzaro reaction.

Among the novel reactions of formaldehyde may now be included its combination with hydrogen phosphide<sup>30</sup> in presence of hydrochloric acid, giving a compound of the type  $\text{PCl}(\text{CH}_2\cdot\text{OH})_4$  which is crystalline. Other combinations of phosphorus compounds with aldehydes and ketones are already known, and it is noteworthy that these are readily formed by the agency of phosphorus trihalide.

Reactions which lead to the synthesis of acetaldehyde or acetic acid from acetylene continue to be actively investigated, and minor advances in technique have been recorded during the year. Variations of catalysts or the media in which they function represent the general lines of inquiry, and a difficulty has been overcome by utilising steam for the effective removal of the acetaldehyde before it has had opportunity to form condensation complexes *in situ*. In favourable circumstances, the yield of aldehyde approaches 80 per cent. The yield of acetaldehyde in the ordinary

<sup>27</sup> A. M. Clover, *J. Amer. Chem. Soc.*, 1922, **44**, 1107; *A.*, i, 619.

<sup>28</sup> Ph. Malvezin, Ch. Rivalland, and L. Grandchamp, *Compt. rend.*, 1921, **173**, 1180; *A.*, i, 8.

<sup>29</sup> Ph. Malvezin, *Ind. Chimique*, 1921, **8**, 311, from *Chem. Zentr.*, 1921, **iii**, 1118; *A.*, i, 222.

<sup>30</sup> A. Hoffman, *J. Amer. Chem. Soc.*, 1921, **43**, 1684; *A.*, i, 8.

laboratory preparation<sup>31</sup> from alcohol is similarly enhanced by the simple device of stirring the chromate mixture in order to disengage the aldehyde rapidly from the solution.

Since the initiation of the Fernbach-Weizmann fermentation process for the production of acetone, numerous attempts have been made to devise uses for the *n*-butyl alcohol which is the accompanying by-product. Several claims consequently appear in the patent literature describing the conversion of this alcohol into butaldehyde and butyric acid, and doubtless similar cheap and useful reagents will be made available.

The older methods for the reduction of acid chlorides to aldehydes were superseded by the procedure introduced by Rosenmund several years ago. It is satisfactory to find that the variability in the efficiency of the nickel and palladium catalysts in his earlier work has been largely overcome and a more trustworthy procedure is available. Extension of this work by Rosenmund and his collaborators to the dialdehydes<sup>32</sup> is illustrated by the case of sebacicdialdehyde,  $C_8H_{16}(CH_2O)_2$ , which is obtainable in a yield of 80 per cent. by the use of hydrogen in presence of palladised kieselguhr and "sulphured" quinoline. Direct formation of acetals proceeds smoothly by careful adjustment of conditions, and it is noteworthy that ammonium chloride functions equally with hydrogen chloride as a catalyst in this connexion.<sup>33</sup> Neutralisation of the acid with sodium ethoxide before isolation of the product has certain advantages over the earlier practice.

Studies on keto-enolic tautomerism which owe so much to the work of Knorr and his collaborators have been amplified by the introduction of interesting examples. As was to be expected, the weapons with which earlier attacks on this problem were made are not found to be generally applicable, and neither the coloration with ferric chloride nor the bromine titration method of K. H. Meyer is useful in all cases for the diagnosis of enol forms.<sup>34</sup> The vagaries of enolisation are responsible for many reactions which are imperfectly understood, and it excites no surprise to learn that diacetylacetone<sup>35</sup> has not the usually accepted open-chain formula. Reactions of acetylacetone with tellurium and selenium tetrachlorides reveal very strikingly the residual affinity of such compounds, and the elegant researches of Morgan, Drew, and

<sup>31</sup> C. E. Adams and J. Williams, *J. Amer. Chem. Soc.*, 1921, **43**, 2420; *A.*, **i**, 222.

<sup>32</sup> K. W. Rosenmund, F. Zetzsche, C. Flütsch, and F. Enderlein, *Ber.*, 1921, **54**, [B], 2888; *A.*, **i**, 39; *ibid.*, 1922, **55**, [B], 609; *A.*, **i**, 431.

<sup>33</sup> R. D. Haworth and A. Lapworth, *T.*, 1922, **121**, 76.

<sup>34</sup> H. P. Kaufmann, *Ber.*, 1922, **55**, [B], 2255; *A.*, **i**, 985.

<sup>35</sup> J. N. Collie and Amy A. B. Reilly, *T.*, 1922, **121**, 1984.

Barker<sup>36</sup> elucidate a recondite problem. The work of J. F. Thorpe, C. K. Ingold, and their collaborators traverses the whole field of tautomeric change, and it is impossible to deal adequately with a subject of these dimensions within the confines of this Report.

Pyrogenic decomposition of acetone<sup>37</sup> leads almost exclusively to scission into keten and methane, and ultimately from the keten into carbon monoxide and ethylene, whilst with higher ketones both saturated and ethylenic hydrocarbons are formed by gain or loss of hydrogen by the radicles at the moment of disruption. Such data are of value in controlling the process of acetone manufacture from calcium acetate. Union of nitrosyl chloride with a normal paraffin in sunlight illustrates a novel and indirect means of oxidation, since heptane, passing through the stages of dipropyl-nitrosomethane and the isomeric oxime, is converted into dipropyl ketone.<sup>38</sup> Auto-oxidation is a phenomenon which has been investigated closely, with special reference to the inhibitory effects of many phenolic compounds.<sup>39</sup> Quinol, especially, suppresses the auto-oxidation of crotonaldehyde even when the "anti-oxygen" is present in so slight an amount as 1 : 100,000.

#### *Acids and their Derivatives.*

Several papers dealing with hydrocyanic acid reflect the interest which attaches to its synthesis from materials of a widely different nature, and its trimeride appears to be represented by aminodicyanomethane. The question has been reopened as to the existence of the tautomeric form, HNC, in equilibrium with the normal nitrile form and evidence of this tendency is adduced.<sup>40</sup> Standard reactions for the preparation of formic, oxalic, acrylic, maleic, and fumaric acids have been revised, and a convenient method of obtaining pure methyl acetate is provided by digestion of 70 per cent. acetic acid with methyl oxalate. The behaviour of acids in ultra-violet light forms the subject of several papers, the halogen acids displaying a marked capacity to decompose into paraffin halides.

Great importance attaches to the precise regulation of conditions for the  $\alpha$ -bromination of acids. The Hell-Volhard method leads to variable results in different instances, and a new series of experi-

<sup>36</sup> G. T. Morgan, H. D. K. Drew, and T. V. Barker, *T.*, 1922, **121**, 922, 2432; compare W. Madelung, *Annalen*, 1922, **427**, 35; *A.*, ii, 344.

<sup>37</sup> (Mlle) E. Peytral, *Bull. Soc. chim.*, 1922, [iv], **31**, 122; *A.*, i, 222; *A. Mailhe, ibid.*, 863; *A.*, i, 985.

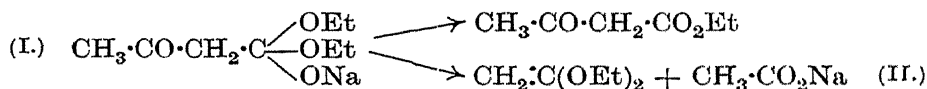
<sup>38</sup> E. V. Lynn and O. Hilton, *J. Amer. Chem. Soc.*, 1922, **44**, 645; *A.*, i, 417.

<sup>39</sup> C. Moureu and C. Dufraisse, *Compt. rend.*, 1922, **175**, 127; *A.*, i, 824.

<sup>40</sup> Edith H. Usherwood, *T.*, 1922, **121**, 1604.

ments<sup>41</sup> substantiate the theories of Aschan and others that the reaction consists essentially in the addition of bromine to an enolic form of the acid, followed by loss of hydrogen bromide, and these conditions are attained by using molecular proportions of bromine along with 2 per cent. of red phosphorus. Traces of water in the acids, or the acids themselves, serve to generate sufficient hydrogen bromide to promote enolisation, a condition which has been followed in another connexion by Lapworth. Bromination of ethyl acetoacetate under conditions resembling those of gaseous chlorination leads to the  $\alpha$ -bromo- instead of the  $\omega$ -bromo-compound.<sup>42</sup> The expense attending the use of ethyl  $\beta$ -iodopropionate as a synthetic agent is obviated by substituting in its place the esters of  $\beta$ -chloro- and  $\beta$ -bromo-propionic acids which are now obtainable from trimethylene glycol, the latter being a by-product from the glycerol fermentation of sugars.<sup>43</sup>

A new explanation, differing from that of Claisen, for the acetoacetic ester synthesis is furnished by an interesting paper<sup>44</sup> describing the isolation of ketenacetal (II), as the result of spontaneous decomposition of the primary product in ethereal suspension, or by the action of water. It is suggested that the first product of the condensation is the compound (I), which changes as described above or is decomposed by dilute acids to give ethyl acetoacetate :



The publication of other confirmatory evidence is promised, and will be awaited with interest.

Addition of hydrogen cyanide to ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate and its homologues occurs readily on treatment of the esters with an aqueous alcoholic solution of potassium cyanide or with hydrogen cyanide containing sufficient of its potassium salt to ensure the presence of cyanogen ions.<sup>45</sup> With simple  $\alpha\beta$ -unsaturated esters such as ethyl crotonate or dimethylacrylate, the additive reaction proceeds smoothly with the formation, after hydrolysis, of substituted succinic acids,<sup>46</sup> and similar products may be obtained from aldehydes by a simplified procedure involving the use of potassium cyanoacetate.

<sup>41</sup> C. F. Ward, *T.*, 1922, **121**, 1161.

<sup>42</sup> L. I. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 216; *A.*, i, 318.

<sup>43</sup> C. A. Rojahn, *Ber.*, 1921, **54**, [B], 3115; *A.*, i, 105.

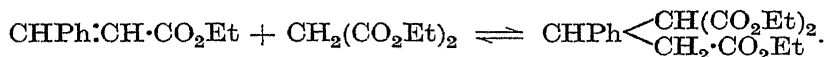
<sup>44</sup> H. Scheibler and H. Ziegner, *ibid.*, 1922, **55**, [B], 789; *A.*, i, 426.

<sup>45</sup> E. Hope and W. Sheldon, *T.*, 1922, **121**, 2223.

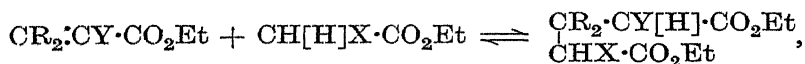
<sup>46</sup> Lucy Higginbotham and A. Lapworth, *ibid.*, 49; *A.*, Lapworth and J. A. McRae, *ibid.*, 1699.

Böeseken has extended his boric acid method of investigating configuration by applying it to acids of different types. Mono-substituted  $\alpha$ -hydroxy-acids,  $\text{OH}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ , show an increase in conductivity in boric acid solutions, but this increase is greater than with disubstituted acids,  $\text{OH}\cdot\text{CRR}'\cdot\text{CO}_2\text{H}$ , and this serves to differentiate the two types. The attainment of this result is attributed to the space relation of the hydroxyl groups. It is suggested that in aqueous solution the carboxyl group is hydrated to  $-\text{C}(\text{OH})_3$ , and in concentrated solution  $\alpha$ -keto-acids contain the residue  $-\text{C}(\text{OH})_2\cdot\text{C}(\text{OH})_3$ . Careful perusal of the systematic summary of the results which have been accumulated up to date will be well repaid.<sup>47</sup>

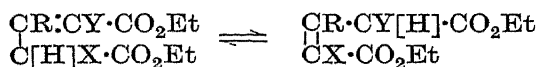
Speculation as to the mechanism of an important group of reactions investigated by Thorpe, Ingold, and their colleagues continues to receive experimental fulfilment. Although the Reporter can do little more within the allotted space than refer the reader to the original papers, mention should be made of the discovery that the Michael condensation is a reversible reaction. The first recorded example of the Michael reaction was the condensation of ethyl sodiomalonate with ethyl cinnamate :



The reaction proceeds from left to right, giving a yield of 35 per cent. of the product. If, however, the product after isolation is submitted to the heating conditions which promote its formation, it is found that the reaction proceeds from right to left to the extent of 60 per cent., about 35—40 per cent. only remaining unchanged. The results furnish decisive evidence in this and other cases that a definite equilibrium is reached determining the amount of the condensation product which may be isolated from the Michael reaction.<sup>48</sup> In general, the change may be represented



and it is suggested that this bears a striking resemblance to the three-carbon tautomerism of substituted glutaconic esters, so that the latter change may be regarded as an intramolecular Michael condensation :

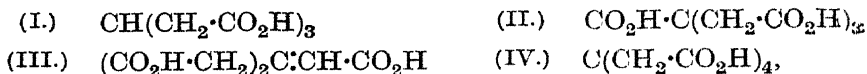


<sup>47</sup> L. Böeseken, *Rec. trav. chim.*, 1921, **40**, 553; *A.*, 1921, i, 843.

<sup>48</sup> C. K. Ingold and Powell, *T.*, 1921, **119**, 1976; C. K. Ingold, E. A. Perren, and J. F. Thorpe, *ibid.*, 1922, **121**, 1765.



A series of researches on the synthesis of the polyacetic acids of methane has reached completion and has resulted in the isolation of all the four compounds,



which may empirically be considered as derivable from glutaconic acid.<sup>49</sup>

The isomerism of the glutaconic acids and their derivatives is represented by an ever-growing literature, and the elucidation of this subject owes much to the work of Thorpe and Ingold. Feist and his co-workers have failed to obtain the *cis*- and normal forms of  $\beta$ -phenyl- $\alpha$ -methylglutaconic acid described by Thorpe and Wood in 1913, but have confirmed the isolation of the *trans*-form and also of a new isomeride which is described as the true *cis*-modification. Feist's general conclusions<sup>50</sup> favour the view that the glutaconic acid series conforms to the ordinary type of geometric isomerism represented by maleinoid and fumaroid forms, and that any apparent variation is one of degree and not of principle.

An interesting study of the formation and properties of  $\beta$ -lactones suggests the speculation that these compounds occur more commonly than is usually supposed.<sup>51</sup> Since the hydrolysis of  $\beta$ -lactones is not a reversible change, they are conveniently derived from  $\beta$ -halogenated acids by hydrolysis in neutral solution.

A large number of papers deal with the relationships of the complex fatty acids, and the following facts emerge. The so-called rapic acid is identical with oleic acid. A new acid isolated from peat by Aschan and named humocerac acid is not identical with lignoceric acid from beechwood tar, since the latter is now shown to be tetracosic acid. It is obtained on oxidising cerebronic acid, which is itself an  $\alpha$ -hydroxypentacosic acid and does not contain a normal chain. Holde and his co-workers have isolated pure erucic acid, and the anhydrides of both this and brassidic acid and also those of the fatty acids of linseed oil have been prepared. The positions of the double linkings in linoleic acid are allocated by a study of sativic acid (tetrahydroxystearic) involving progressive elimination of the hydroxyl groups, and the constitution of sativic acid is determined by alkali fusion. Caution, however, should be observed in view of the instances of a benzylic acid transformation which are known to occur under this treatment,

<sup>49</sup> C. K. Ingold and L. C. Nickolls, *T.*, 1922, 121, 1638.

<sup>50</sup> F. Feist, *Annalen*, 1922, 428, 25, 59, 68; *A.*, i, 521.

<sup>51</sup> H. Johansson and S. H. Hagman, *Ber.*, 1922, 55, [B], 647; *A.*, i, 425.

Electrosynthesis of azelaic and thapsic acid <sup>52</sup> has been achieved, and it is now clear that the latter is identical with *n*-tetradecanedicarboxylic acid.

### *Halogen Compounds.*

A greatly increased yield of methyl bromide is obtainable by a modified procedure <sup>53</sup> which eliminates the usual risk of the production of flame. The usual mixture of methyl alcohol and red phosphorus should preferably be boiled for fifteen minutes before the addition of bromine to the gently boiling liquid. When bromine is mixed with methylal in a freezing mixture, the chief products are methyl bromide and dibromomethylal,  $\text{CBr}_2(\text{OMe})_2$ . The latter is an effective methylating agent, readily converting aniline into methylaniline, sodium cinnamate into the methyl ester,  $\beta$ -naphthol into the ether, and sodiomalonic ester into the substitution derivative.<sup>54</sup> A convenient preparation of vinyl halides *in situ* is rendered possible by distilling concentrated halogen acids in presence of calcium carbide while simultaneously saturating the mixture with the gaseous hydrogen halide. Certain metallic chlorides act as accelerators, but ferric chloride promotes the formation of dichloroacetaldehyde.<sup>55</sup> Chloroacetyl chloride has been obtained by the catalytic oxidation of chlorinated ethylene, and this reagent has been applied with success in the preparation of cellulose esters.<sup>56</sup> Various catalytic processes leading to the polychloroethanes from acetylene have been described. Arsenic trichloride combines additively with acetylene to give the primary, secondary, and tertiary  $\beta$ -chlorovinylarsines, which readily undergo oxidation to the corresponding derivatives of arsenic acid. Such compounds are reminiscent of the reactions which lead to the formation of  $\beta\beta'$ -dichlorodiethyl sulphide, and it is satisfactory to observe that the same authors <sup>57</sup> have resolved many doubts as to the nature of the reaction between ethylene and the sulphur chlorides and have revealed the identity of the related products isolated by other workers. Hydrolysis of "mustard gas" with alcoholic potassium hydroxide <sup>58</sup> gives rise to divinyl sulphide, which again forms a dichloride with hydrochloric acid, but this product is the  $\alpha\alpha$ -dichloro-compound and is a non-vesicant, as

<sup>52</sup> Mabel Carmichael, *T.*, 1922, **121**, 2545.

<sup>53</sup> W. Steinkopf and G. Schwen, *J. pr. Chem.*, 1921, [ii], **102**, 363; *A.*, 1921, i, 841.

<sup>54</sup> F. Feist, *Z. angew. Chem.*, 1922, **35**, 489; *A.*, i, 912.

<sup>55</sup> Brit. Pat. 156120; *A.*, i, 517.

<sup>56</sup> W. L. Barnett, *J. Soc. Chem. Ind.*, 1921, **40**, 286; *A.*, i, 232; and D.R.-P. 340872.

<sup>57</sup> F. G. Mann and Sir W. J. Pope, *T.*, 1922, **121**, 1754, 594.

<sup>58</sup> S. H. Bales and S. A. Nickelson, *ibid.*, 2137.

indeed is the oxygen analogue of mustard gas, the isolation of which is recorded.

Robinson's theory of the induced polarity of atoms has stimulated inquiry as to the labile character of certain groups in a selected series of compounds. In several papers, A. K. Macbeth and his collaborators<sup>59</sup> have studied this problem in great detail, and their general method of investigation is to submit selected halogen compounds, among others, to the action of a definite range of reducing agents and measure by volumetric methods the nature and extent of the reducing action. Certain halides readily lose their halogen atoms under these conditions, and their labile character is attributed to the development of positive polarity by reason of the position such atoms occupy in relation to other groups. The suggestion that bromomalonate esters owe the labile nature of the halogen to the presence of an oxygen-halogen linking appears to be at variance with the results obtained by a comparison of the absorption spectra of such compounds with those of ethyl malonate. The results recorded find a reasonable explanation in the theory which the authors have adopted.

On the other hand, Gupta and Thorpe<sup>60</sup> find this explanation unacceptable in the cases which they have examined and prefer the tautomeric hypothesis which correlates the labile character of halogen atoms in selected carbon compounds with the tendency of the latter to acquire a hydrogen atom so located as to promote enolisation, and their theory is supported by other workers.

#### *Optical Activity.*

An almost unique case of the optical activation of a racemic compound is afforded by the observation that on mixing *l*-malic acid with solutions of the alkali salts of racemic acid *d*-tartaric acid is liberated.<sup>61</sup> A parallel example is furnished by *dl*-phenyl-methylcarbinol, which undergoes catalytic dehydration in the presence of 1 per cent. of camphorsulphonic acid at 100° with the formation of the *l*-ævorotatory ether oxide, whilst the unchanged carbinol was also activated.<sup>62</sup> Rather different in principle is the procedure adopted for the activation or partial resolution of *dl*-mandelic acid. The *l*-menthyl ester on chlorination with thionyl chloride, followed by hydrolysis, gives rise to *l*-phenylchloroacetic acid.<sup>63</sup> The practice of separating optical isomerides by fractional

<sup>59</sup> T. Henderson and A. K. Macbeth, *T.*, 1922, 121, 892; E. L. Hirst and A. K. Macbeth, *ibid.*, 904; H. Graham and A. K. Macbeth, *ibid.*, 1109.

<sup>60</sup> B. M. Gupta and J. F. Thorpe, *ibid.*, 1896.

<sup>61</sup> A. McKenzie and Nellie Walker, *ibid.*, 349.

<sup>62</sup> H. Wuyts, *Bull. Soc. chim. Belg.*, 1921, 30, 30; *A.*, 1921, i, 506.

<sup>63</sup> A. Shimomura and J. B. Cohen, *T.*, 1921, 119, 1818.

crystallisation of their salts was illustrated in the case of lactic acid by Purdie. An extension of this procedure to organic esters has demonstrated that *l*-menthyl esters of atrolactic acid and  $\alpha$ -hydroxy- $\beta$ -phenylpropionic acid are resolvable by crystallisation from solvents,<sup>64</sup> since on hydrolysis of the crystals the active acids are isolated. The usual practice for the resolution of racemic compounds is generally regarded as too difficult an exercise to be handled by a student as a laboratory preparation, but the simplified manipulation described by Kenner in the case of methyl-*n*-hexyl-carbinol incidentally overcomes this objection,<sup>65</sup> and provides an easy access to a useful optically active alcohol.

Synthesis of optically active compounds by methods which involve activation simultaneously with the creation of the system of groupings responsible for asymmetry is the only genuine kind of asymmetric synthesis. The following recent examples<sup>66</sup> appear to come within this category: the cyanohydrin synthesis applied to isovaleraldehyde and *p*-tolualdehyde in presence of emulsin gives rise to dextrorotatory nitriles; yeast fermentation in presence of pyruvic acid or of acetylcarbinol leads to optically active acetylmethyl-carbinol or *l*-propylglycol, respectively.

The discovery of Franchimont that ethyl tartrate is a crystalline solid with a freezing point of  $18.7^{\circ}$  has contributed a new criterion of purity, and the admirable investigations<sup>67</sup> based on material conforming to this new standard have resulted in a series of re-determinations of specific rotation, density, refractive index, and dispersion, using light of representative wave-lengths. The observed specific rotations range from  $+6.87^{\circ}$  in the green to  $-12.2^{\circ}$  for the last photographic reading in the ultra-violet and include thirty-four values for the intermediate lines of the spectrum. The rotatory dispersion is in close agreement with that calculated by using two terms of the Drude equation. Comparative measurements of the interfacial tension between aqueous solutions of the two active tartaric acids and racemic acid in contact with inert liquids reveal no differences for the *d*- and *l*-forms, but a marked divergence from this value for racemic acid, and this is adduced as evidence of the existence in solution of the racemic acid molecule. On increasing the dilution, there is a clear indication of dissociation into *d*- and *l*-forms. It is demonstrated that the type of union found in racemic acid is not restricted to the two antipodes, since a like combination may be artificially produced between

<sup>64</sup> H. Wren and E. Wright, *T.*, 1921, **119**, 798.

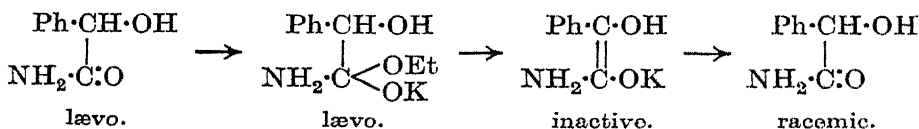
<sup>65</sup> *T.*, 1922, **121**, 2540.

<sup>66</sup> L. Rosenthaler, *Fermentforsch.*, 1922, **5**, 334; *A.*, i, 480; J. Hirsch, *Biochem. Z.*, 1922, **131**, 178; *A.*, i, 973. Compare *A.*, 1921, i, 150.

<sup>67</sup> T. M. Lowry and J. O. Cutter, *T.*, 1922, **121**, 532.

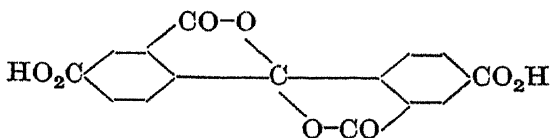
*d*- and *i*-tartaric acid, the complex containing one molecule of each acid along with water of crystallisation as in racemic acid, the rotatory power being thereby halved.<sup>68</sup>

Evidence is available which disposes of the assumption that racemisation of *l*-mandelamide with alkali is to be attributed to enolisation. An explanation which is supported by experiment<sup>69</sup> is that alkali or potassium ethoxide combines additively with the amide as in the Claisen reactions, subsequent loss of water or alcohol producing an inactive compound. The changes may be expressed :



The racemisation of the mandelonitrile residue in amygdalin is explicable on a similar principle. The presence of a migrational hydrogen atom on the asymmetric carbon atom appears to lead in all such cases to racemisation; this tendency is suppressed by substitution of a methyl group for the hydrogen atom or alternatively by replacing the phenyl residue by benzyl. On the other hand, the tendency is increased by the presence of a methoxyl or tolyl group in place of the hydroxyl group attached to the asymmetric carbon atom.

Of the many examples of resolution into optically active forms which have been communicated during the period under review, one of the most interesting<sup>70</sup> is that of the keto-dilactone of benzo-phenone-2 : 4 : 2' : 4'-tetracarboxylic acid shown below :



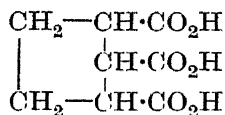
The compound affords another example of the existence of optical enantiomorphs containing no asymmetric atom. Theoretically, the molecule is divisible at the central spirane carbon atom into two identical halves, but the molecular asymmetry is attributable to the fact that these two halves lie in different planes which meet and intersect at right angles at this central atom. The resolution has been achieved by the use of *l*- $\alpha$ -phenylethylamine. Taking

<sup>68</sup> Ph. Landrieu, *Bull. Soc. chim.*, 1922, **33**, 667; *A.*, i, 808; S. W. Penny-quick, *J. Amer. Chem. Soc.*, 1922, **44**, 1133; *A.*, i, 624.

<sup>69</sup> A. McKenzie and Isobel A. Smith, *T.*, 1922, **121**, 1348.

<sup>70</sup> W. H. Mills and C. R. Nodder, *ibid.*, 1921, **119**, 2094.

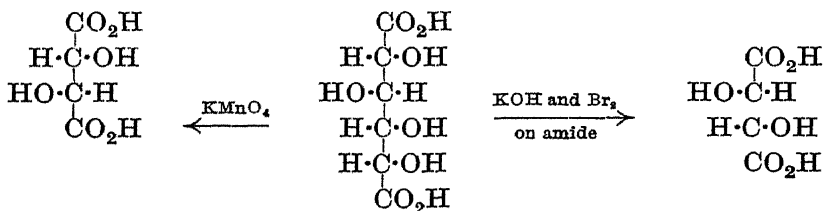
advantage of the existence of  $\alpha\alpha'$ -dibromoadipic acids in both *meso*- and *racemic* forms, W. H. Perkin and E. Robinson<sup>71</sup> have condensed the esters of these acids with ethyl malonate in order to synthesise the geometric isomerides of *cyclopentane-1 : 2 : 3*-tricarboxylic acid :



Two of these isomerides, the *cis-trans-cis*, and the *cis-cis-cis*, are *meso*-forms and a third, the *cis-trans-trans*, is a *racemic* form, which was resolved by means of brucine.

### Carbohydrates.

*Monosaccharides*.—Improved methods for the preparation of a number of sugars and their derivatives are reported in the literature of the year, among which are included fructose, mannose, galactose, raffinose, sorbitol, inulin, and gluconic acid. Scrutiny of the procedure involved in the oxidation of hexoses has revealed an unexpected result. At the ordinary temperature and in the absence of air, nitric acid transforms glucose or gluconic acid into  $\alpha$ -keto-gluconic acid, in the formation of which the oxidation of a secondary alcohol group is involved.<sup>72</sup> Fischer's degradation of *d*-saccharic acid by oxidation with permanganate into *d*-tartaric acid proved the configuration of the groups attached to the second and third carbon atoms of the glucose chain. The diamide of *d*-saccharic acid yields, however, *l*-tartaric acid through the related dialdehyde on treatment with bromine and potassium hydroxide,<sup>73</sup> and this proves the configuration of the groups attached to carbon atoms 3 and 4.



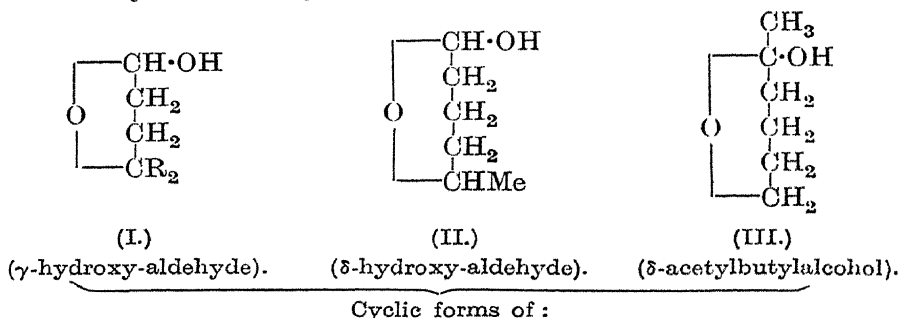
Collateral evidence bearing on the character of the oxide linking in simple hexoses is furnished by the synthesis of  $\gamma$ - and  $\delta$ -hydroxy-

<sup>71</sup> *T.*, 1921, 119, 1392.

<sup>72</sup> H. Kiliani, *Ber.*, 1922, 55, [B], 75, 493; *A.*, i, 223, 321.

<sup>73</sup> M. Bergmann, *ibid.*, 1921, 54, [B], 2651; *A.*, i, 7.

aldehydes and -ketones.<sup>74</sup> The location of the hydroxyl group with reference to the aldo- or keto-group resembles that of a sugar, and it is significant that these compounds simulate the reactions of sugars. They form "glucosides" or semi-acetals with methyl-alcoholic hydrogen chloride, instead of the usual acetals, and the ease of hydrolysis of these methyl derivatives is comparable with that of the glucosides. Moreover, the typical aldehyde reactions, although not altogether suppressed, are modified or retarded by reason of the existence of the aldehydes or ketones in their more stable butylenc- or amylene-oxidic forms :



The methyl semi-acetal of III contains an amylene oxide ring and the sensitiveness of this analogue of methylfructoside towards extremely dilute acids is reminiscent of the behaviour of the  $\gamma$ -glucosides or fructosides. Should the amylene-oxidic structure be assigned to the  $\gamma$ -sugars, this characteristic property will receive sufficient explanation from the analogy which has been drawn.

A re-investigation of the acetone derivatives of glucose indicates that their structure conforms to the  $\gamma$ -glucose type, and formulæ are ascribed to those compounds which represent  $\gamma$ -glucose by a propylene-oxidic structure. On the other hand, both fructose mono- and di-acetones are derivatives of ordinary levorotatory or butylene-oxidic fructose, and it is remarkable that the same compounds are formed either from ordinary fructose or  $\gamma$ -methylfructoside.<sup>75</sup>

The chemistry of glucosamine has been advanced by the recognition and study of the new  $\beta$ -form, and a comparison of its molecular rotation with that of the  $\alpha$ -form shows that these values are in agreement with Hudson's rule if glucosamine is accepted as 2-aminoglucose, and at variance with its relationship to mannose.

<sup>74</sup> B. Helferich and M. Gehrke, *Ber.*, 1921, 54, [B], 2640; *A.*, i, 9; B. Helferich and T. Malkomes, *ibid.*, 1922, 55, [B], 702; *A.*, i, 431; M. Bergmann and A. Miekeley, *ibid.*, 1390; *A.*, i, 618.

<sup>75</sup> J. C. Irvine and J. Patterson, *T.*, 1922, 121, 2146.

Since glucosamine has been converted into both glucose and mannose, the latter change must involve a Walden inversion. Condensation of triacetyl bromoglucosamine with salicylaldehyde does not occur through the phenolic group of the latter to give a glucoside, but involves a union of the aldehyde residue of salicylaldehyde with the amino-group of the sugar. The bromine atom in the reducing position in the sugar derivative thus remains intact, and is removed by solution in alcohols and leads to glucoside formation. The latter reaction is accompanied by a gradual change of rotation which, in the absence of precise knowledge of the structure of the salicylidene derivative, was formerly described as pseudo-mutarotation. Whilst serving to elucidate an apparent anomaly in the optical behaviour of a supposed glucoside, this research <sup>76</sup> furnishes additional evidence of the tendency of glucosamine to form derivatives of the betaine-ring type. Thus, whilst triacetyl methylglucosamine combines to give an 80 per cent. yield of the salicylidene derivative and presumably exists largely as an amino-hexose complex, the de-acetylated methylglucosamine yields only 26 per cent. of the salicylidene product, the inference being that free methylglucosamine exists mainly in the betaine form in which the glucosidic methyl group is united with nitrogen, giving the

cyclic complex :  $\begin{array}{c} \text{---CH---O---Me} \\ | \quad \diagdown \quad / \\ \text{CH---N---H} \\ | \quad \diagup \quad \backslash \\ \quad \quad \text{H} \end{array}$  . The capacity of glucosamine to

condense with reagents varied in type is also illustrated by its transformation into crystalline heterocyclic compounds of the glyoxaline and pyrrole class in presence of potassium thiocyanate or silver cyanate,<sup>77</sup> reactions which bear a resemblance to the first stage in Pyman's synthesis of histidine. The idea that glucose, reacting as an aldehyde, gives a glucose-ammonia which is an analogue of aldehyde-ammonia is revived,<sup>78</sup> but, on the other hand, it is confirmed that glucose-anilide has the butylene-oxidic structure and is therefore aniline-glucoside.<sup>79</sup>

*Glucosides and Disaccharides.*—The recognition of the sugar residue in amygdalin has long been a subject of dispute and Fischer's tentative suggestion that the biose may be identical with maltose has often been misconstrued. The methylation of amygdalin has been accomplished by means of methyl sulphate and sodium hydroxide, giving the completely methylated amygdalinic ester.<sup>80</sup>

<sup>76</sup> J. C. Irvine and J. C. Earl, *T.*, 1922, 121, 2370, 2376.

<sup>77</sup> H. Pauly and E. Ludwig, *Z. physiol. Chem.*, 1922, 121, 170; *A.*, i, 953.

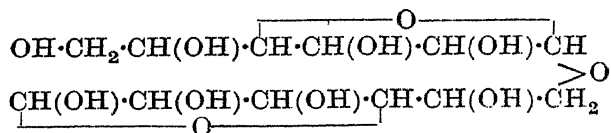
<sup>78</sup> A. R. Ling and D. R. Nanji, *T.*, 1922, 121, 1682; *J. Soc. Chem. Ind.*, 1922, 41, 151r; *A.*, i, 631.

<sup>79</sup> T. Sabalitschka, *Ber. deut. Pharm. Ges.*, 1921, 31, 439; *A.*, i, 247.

<sup>80</sup> W. N. Haworth and Grace C. Leitch, *T.*, 1922, 121, 1921.



Hydrolysis of this compound led to the isolation of butylene-oxidic forms of 2:3:5-trimethyl glucose and 2:3:5:6-tetramethyl glucose, from which it follows that the amygdalin-biose has the same structural formula as maltose :



The stereochemical formula is, however, probably different from that of maltose, and the biose is most likely a glucose- $\beta$ -glucoside of the above structure, and may prove to be identical with *iso*-maltose or gentiobiose.

Progress has been made in several researches on the constitution of digitonin, which is shown to contain both hexose and pentose residues. The difficult problem of the constitution of the saponins, whilst continuing to engage the attention of chemists, requires exceptional patience and resource, and it would seem that greater success can only be attained by an extended study of the crystalline sapogenins, which are related to the terpenes.<sup>81</sup> The glucose residue in indican appears to be of the normal butylene-oxide type.<sup>82</sup>

A biochemical synthesis of  $\alpha$ -methylmannoside is reported<sup>83</sup> and also the synthesis of new condensation complexes from helicin.

*Polysaccharides*.—A significant feature of the work of the year is the unprecedented volume of researches on the constitution of the polysaccharides. It is only possible to reflect the general trend of the published results, which are often so contradictory that little finality is to be expected at the present stage. Starch, when degraded by bacteria, gives rise to a series of products, many of them crystalline, which are represented by a formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , where  $n$  is a small integer such as 2, 3, 4, 6, 8, and these compounds are known as the di-, tri-, tetra- (etc.) amyloses. In relation to starch itself, these are comparatively simple substances, and their investigation may obviously be expected to throw some light on the structure of starch. On distilling potato-starch in glycerol, a new depolymerised product is isolated, differing from the above triamylose, but isomeric with it, and this is named trihexosan.<sup>84</sup>

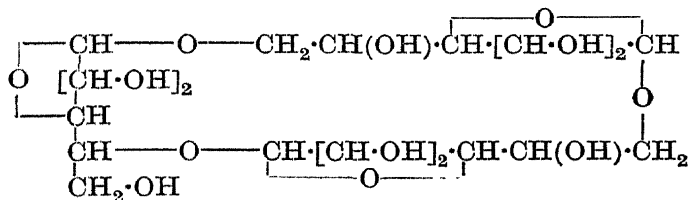
<sup>81</sup> A. Windaus and K. Weil, *Z. physiol. Chem.*, 1922, **121**, 62; *A.*, i, 848; A. W. van der Haar, *Rec. trav. chim.*, 1921, **40**, 542; *A.*, 1921, i, 877.

<sup>82</sup> A. K. Macbeth and J. Pryde, *T.*, 1922, **121**, 1660.

<sup>83</sup> H. Hérissé, *Compt. rend.*, 1921, **173**, 1406; *A.*, i, 112; R. de Fazi, *Gazzetta*, 1922, **52**, i, 429; *A.*, i, 755.

<sup>84</sup> A. Pictet and R. Jahn, *Helv. Chim. Acta*, 1922, **5**, 640; *A.*, i, 987.

Pringsheim, Karrer, and others have resorted to the use of a combination of the Purdie reaction and the methyl sulphate method of methylation in a detailed study of these depolymerised starches and, coupled with the application of acetylating agents, have endeavoured to trace the simplest depolymerised unit of which the starch molecule is composed. This is variously regarded as  $(C_6H_{10}O_5)_2$  or  $(C_6H_{10}O_5)_3$ . A. Pictet has abandoned his opinion that starch is polymerised  $\beta$ -glucosan, and, along with Pringsheim, regards  $(C_6H_{10}O_5)_3$  as the unit of starch. Karrer, on the contrary, considers that the unit is a diamylose, namely, anhydromaltose,<sup>85</sup> since all methods of degrading starch had hitherto led to maltose or polymeric forms of its anhydride. Methylation of purified rice-starch with methyl sulphate yields a product which is incompletely methylated and on hydrolysis gives rise to two parts of dimethyl glucose and one part of 2 : 3 : 6-trimethyl glucose, a result which suggests the view that the starch unit is a trihexosan, and that the partly methylated starch (OMe = 37 per cent.) contains in each unit a trimethyl hexose residue and two dimethyl hexose residues. A structural formula<sup>86</sup> is based upon these results :



This formula takes into account the constitution already assigned to maltose,<sup>87</sup> and it is noteworthy that Karrer's anhydromaltose formula does not admit of the formation of the 2 : 3 : 6-trimethyl glucose which has been isolated as above. It is pointed out that ordinary starch contains nitrogen and phosphorus in chemical combination, and an ingenious suggestion is advanced<sup>88</sup> that the resistance of part of the starch grain to the action of hot water or acids is due to the presence of condensed complexes of the starch unit with silicic or phosphoric acid or water, the breakdown of which gives rise to the polyamyloses.

In confirmation of earlier work, it is now established that cotton cellulose at least contains only glucose residues.<sup>89</sup> A new di-

<sup>85</sup> P. Karrer and Elizabeth Bürklin, *Helv. Chim. Acta*, 1922, **5**, 181; *A.*, i, 435.

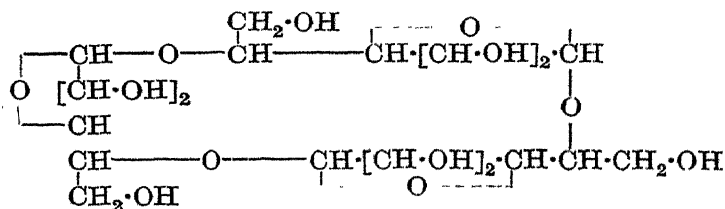
<sup>86</sup> J. C. Irvine and J. Macdonald, *Brit. Assoc. Reports*, 1922.

<sup>87</sup> W. N. Haworth and Grace C. Leitch, *T.*, 1919, **115**, 809.

<sup>88</sup> G. Malfitano and M. Catoire, *Compt. rend.*, 1922, **174**, 1128; *A.*, i, 527.

<sup>89</sup> J. C. Irvine and E. L. Hirst, *T.*, 1922, **121**, 1585.

saccharide, celloisobiose, has been isolated by Ost and Knoth<sup>90</sup> from the products of acetolysis of cellulose. Its physical constants and the solubilities of its octa-acetate differentiate it from cellobiose, and its osazone melts at 165—167°. Although hydrolysable with greater difficulty than cellobiose, its acetate changes into a derivative of the latter sugar. A new degradation of cellulose into a biose-anhydride is reported by Hess,<sup>91</sup> and its tetracthyl derivative may be obtained by acetolysis of ethylated cellulose. Karrer<sup>92</sup> has advanced a cellulose constitution which represents the molecule as composed of two units only of anhydro-cellobiose. It was indicated two years ago by W. S. Denham<sup>93</sup> that methylation of cellulose could be carried to the stage at which three methoxyl groups were introduced into each  $C_6H_{10}O_5$  residue, the methoxyl content being 44.6 per cent. as compared with a theoretical value of 45.6. The later work<sup>94</sup> describes the hydrolysis of methylated cotton cellulose containing  $OMe = 43.0$  per cent., which gave almost entirely the 2 : 3 : 6-trimethyl glucose, thus affording a proof that the glucose residues in  $\alpha$ -cellulose are identical in structure. The above trimethyl glucose has recently been the subject of further study<sup>95</sup> and the structure assigned to it by other workers is confirmed. A formula for the cellulose unit which is based upon these striking results must take into account the yield of cellobiose which is obtainable when cellulose is subjected to acetolysis, and Irvine, Denham, and Hirst suggest among others the following, which for several reasons is preferred :



The interesting observation is made that percolation of salt solutions through cellulose produces an acid filtrate, which suggests the hydrolysis of, in one case, sodium chloride to hydrochloric acid. Aqueous washings from the cellulose so treated give an alkaline solution of alkali content almost equivalent to the acidity

<sup>90</sup> *Cellulosechemie*, 1922, 3, 25; *A.*, i, 526.

<sup>91</sup> K. Hess and W. Wittelsbach, *Ber.*, 1921, 54, [B], 3232; *A.*, i, 116; K. Hess, *ibid.*, 2867; *A.*, i, 12.

<sup>92</sup> P. Karrer, *Cellulosechemie*, 1921, 2, 125; *A.*, i, 231.

<sup>93</sup> W. S. Denham, *T.*, 1921, 119, 77.

<sup>94</sup> J. C. Irvine, W. S. Denham, and E. L. Hirst, *Brit. Assoc. Reports*, 1922,

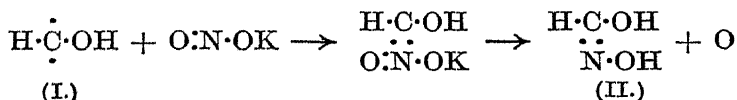
<sup>95</sup> J. C. Irvine and E. L. Hirst, *T.*, 1922, 121, 1213.

of the salt solution. The resultant effect on the cellulose is a matter of considerable importance.<sup>96</sup>

One of the many disconcerting factors encountered in the elucidation of the constitution of polysaccharides is the phenomenon of polymerisation and depolymerisation which may appear at any stage of the work. This circumstance is responsible for the isolation of no fewer than three types of trimethyl inulin, two of which are soluble in ether and show rotations of opposite sign, whilst the third is insoluble in ether. Such apparent anomalies are responsible for the frequent claims and counterclaims of different workers. Genuine progress has, however, been made in that it is finally established<sup>97</sup> that inulin is composed entirely of  $\gamma$ -fructose residues; these may conceivably be arranged in groups of three in the unit formula of the inulin molecule on the analogy of starch and cellulose, namely:  $[(C_6H_{10}O_5)_3]_x$ .

#### *Nitrogen Compounds.*

An inquiry<sup>98</sup> which will be welcomed by all chemists has been initiated with promising results into the mechanism of the synthesis of nitrogenous products in the plant. There is an experimental basis for the belief that the production of activated formaldehyde (I) from carbon dioxide under the influence of light leads, in the presence of nitrites or nitrates, to the synthesis of formhydroxamic acid (II), the photosynthetic formation of which was established by Baudisch,



and that this product enters with remarkable ease into combination with more activated formaldehyde, giving rise to amino-acids and possibly proteins and alkaloids. The progress of this work will be watched with special interest and with the expectancy that sufficient of the laboratory products may be made available for definite characterisation and analysis. Significance is attached to the observation that sustained efforts are in progress to obtain synthetic carbamide on a considerable scale. Scrutiny of the patent literature reveals a noteworthy attempt to replace the laboratory methods by a direct commercial process which will

<sup>96</sup> Helen Masters, *T.*, 1922, **121**, 2026; A. Tingle, *J. Ind. Eng. Chem.*, 1922, **14**, 198; *A.*, i, 434; E. Knoevenagel and H. Busch, *Cellulosechemie*, 1922, **3**, 42; *A.*, i, 636; J. Huebner and F. Kaye, *J. Soc. Chem. Ind.*, 1922, **41**, 94r; *A.*, i, 435.

<sup>97</sup> J. C. Irvine, Ettie S. Steele, and Mary I. Shannon, *T.*, 1922, **121**, 1060.

<sup>98</sup> E. C. C. Baly, I. M. Heilbron, and D. P. Hudson, *ibid.*, 1078.

involve the utilisation of carbon dioxide and ammonia or of cyanamide.

The synthetic utility of cyanamide and dicyanodiamide is emphasised by the numerous examples on record of preparations of guanidine derivatives. The alkylated guanidines are readily available by the interaction of hydrochlorides of alkylamines and dicyanodiamide.<sup>99</sup> The latter reagent combines with ammonium perchlorate to give the explosive guanidonium perchlorate, which provides a convenient source for the preparation of guanidine and its salts.<sup>1</sup> Condensation of ethylene chlorohydrin with cyanamide yields the cyanoamidoethyl alcohol, whence, reacting in the form  $\text{NC}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , guanidoethyl alcohol may be derived by combination with alcoholic ammonia. Although orthocarbonic acid and its amino-analogue have only a hypothetical existence, yet it is interesting to consider a scheme of derivation<sup>2</sup> which proceeds from the formula  $\text{C}(\text{NH}_2)_4$  by progressive loss of ammonia from one or more molecules to guanidine, diguanidine, cyanamide; and from a polymeride of the latter, namely, melamine,  $(\text{H}_2\text{CN}_2)_3$ , to melam, melem, melon, and hydromelonic acid. A new member of the series, dicyanamide,  $(\text{CN})_2\text{NH}$ , is an acid which is comparable in strength with hydrochloric acid.

The synthesis of *s*-aminohydroxysuccinic acid has on several occasions been prematurely reported, but success has now been achieved by heating chloromalic acid under pressure with aqueous ammonia.<sup>3</sup> The acid so attained is a mixture of two crystalline isomerides, which give rise on treatment with nitrous acid to racemic and *meso*tartaric acids. Applications of the aminoethanols which are of service as intermediate products in the synthesis of local anæsthetics, continue to excite interest. Although it is not possible to give an outline of the many synthetic compounds the preparation of which is chiefly described in patents, yet certain novel modes of formation may be summarised. Condensation of  $\alpha$ -bromopropionic acid with dimethylamine and subsequent esterification lead to ethyl  $\alpha$ -dimethylaminopropionate. Reduction of the ester group is effected by sodium in alcohol, and the product is *N*-dimethylalaninol,  $\text{Me}_2\text{N}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ , which readily gives with methyl iodide alanine-choline iodide. The method finds application in a number of cases quoted by Karrer and his pupils.<sup>4</sup> Re-

<sup>99</sup> E. A. Werner and J. Bell, *T.*, 1922, 121, 1790; T. L. Davis, *J. Amer. Chem. Soc.*, 1921, 43, 2230; *A.*, i, 118.

<sup>1</sup> W. Marckwald and F. Struwe, *Ber.*, 1922, 55, [B], 457; *A.*, i, 328; E. Fromm and E. Honold, *ibid.*, 902; *A.*, i, 529.

<sup>2</sup> E. C. Franklin, *J. Amer. Chem. Soc.*, 1922, 44, 486; *A.*, i, 440.

<sup>3</sup> H. D. Dakin, *J. Biol. Chem.*, 1921, 48, 273; *A.*, i, 143.

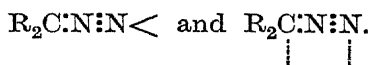
<sup>4</sup> *Helv. Chim. Acta*, 1922, 5, 469; *A.*, i, 813.

placement of the hydroxyl group in diethylaminoethanol by halogen and condensation of this halide with sodio-malonic and -acetoacetic esters represents another line of inquiry which is in progress, whilst the use of Gabriel's phthalimide method in conjunction with the halogenohydrins provides another mode of preparation of amino-alcohols.

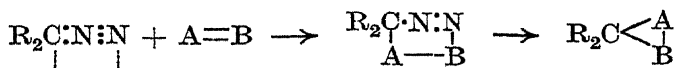
Prolonged heating of mercury fulminate at  $90^{\circ}$  effects an important change without alteration of the crystalline form and gives a non-explosive product which has been named pyrofulmin, but indications point to its not being a homogeneous <sup>5</sup> compound.

In two theoretical papers which merit attention, Staudinger <sup>6</sup> reviews the reactions of ketens and aliphatic diazo-compounds and reaches conclusions which suggest a modification of the constitution of the latter in accordance with the views of Thiele and Angeli.

Compounds of the type  $R_2C:N:N$  are termed azenes on the analogy of the ketens, and two reactive points are indicated :



Reactions occurring at the terminal position, involving the first scheme of formulation, are common, such as reduction of aliphatic diazo-compounds and addition of Grignard reagents. Many reactions, such as the addition of unsaturated compounds, occur in conformity with the second scheme, and may be written :



and the action of water, acids, alcohols, and amines proceeds in a similar manner. Comparison with the reactions of ketens enables a close analogy to be drawn.

The period covered by this division of the Report is from December 1921 to November 1922 inclusive, but the section on optical activity includes also the work of the previous year.

W. N. HAWORTH.

## PART II.—HOMOCYCLIC DIVISION.

IN compiling this report the writer has endeavoured to adopt an impartial and unprejudiced point of view, but he is fully aware of the difficulties which may be encountered in such an attempt and, if there are occasionally signs of straying from the path, the only extenuating circumstance which can be urged in mitigation of the

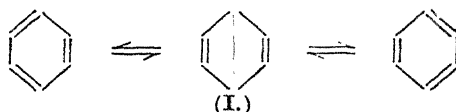
<sup>5</sup> Langhans, *Z. ges. Schiess. u. Sprengstoffw.*, 1922, 17, 9, 18, 26; *A.*, i, 328.

<sup>6</sup> *Helv. Chim. Acta*, 1922, 5, 87; *A.*, i, 238.

offence is that in all probability an entirely neutral survey would also be lifeless and devoid of value. Both in volume and in sustained interest the work published during the year fully reaches the pre-war level and attention may be specially directed to the series of papers on tautomerism, ring-formation, and allied subjects which have been prosecuted in the laboratories at S. Kensington and recorded in papers which followed one another in quick succession with almost bewildering rapidity.

*Constitution of Benzene.*

The Dewar formula for benzene has been revived by C. K. Ingold,<sup>1</sup> who regards it as one of the phases in an equilibrated system of valency isomerides :



The argument is partly by analogy with the recently observed intra-annular tautomers (p. 113) and partly derived from a survey of the reactions of phenol and its derivatives.

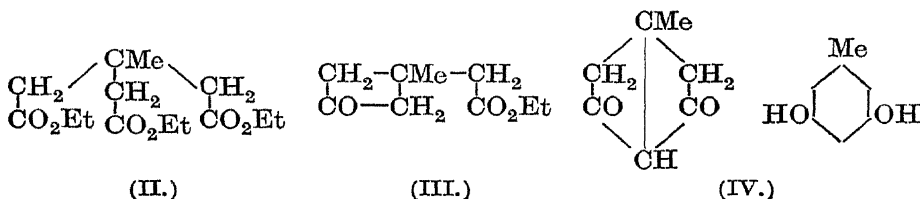
This view would be contested by few if the para-linking were interpreted as amounting to a relatively weak partial valency only, but the suggestion is apparently advanced in a much more uncompromising form, to which there are obvious and serious objections. It is, for example, contrary to experience to assume that a substance of the formula I could be so stable to permanganate as are many derivatives of benzene. There is also the behaviour with ozone, the absence of dicyclic products of reduction processes, and, in general, the absence of any degradation product of benzene or its derivatives in which the carbon atoms in the para-position are found to be connected. It would be beside the mark to answer this criticism by assuming high reactivity of the para-bond, because in that case too high a standard of activity is set by the ethylene linkings. A conjugated system connecting two atoms is in many respects the equivalent of a direct bond and naturally, therefore, very many reactions can equally well be represented as due to the intervention of either. But the theory of reversible addition to conjugated systems involves the fewer inconsistencies and is a wider generalisation. Only one specific point can be touched upon and that concerns the relation of quinol to quinone. The scheme given is :



<sup>1</sup> *T.*, 1922, 121, 1123.

This does not accommodate the fact that dihydric phenols may be oxidised to quinones by means of silver oxide or lead peroxide in dry ethereal or benzene solution,<sup>2</sup> and many other arguments could be quoted in support of the view that the relation between quinol and quinone is a directly reversible one involving the removal and addition of two hydrogen atoms. An extremely elegant synthesis of orcinol is described by Ingold in Part II of the series, the title of which is "Synthetic Formation of the Bridged Modification of the Nucleus."<sup>3</sup>

Ethyl  $\beta$ -methylmethanetriacetate (II) was converted by means of sodium or potassium in xylene solution into a mixture of substances from which it was possible to isolate ethyl 3-methylcyclobutan-1-one-3-acetate (III). The question of the constitution of this substance is not discussed, and it must be assumed that there is some undisclosed reason why it cannot have the open-chain formula,  $\text{Me}\cdot\text{CO}\cdot\text{CH}:\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , apparently a possibility. The ester III was obtained in very small yield and was found to undergo transformation to orcinol (IV) under the influence of sodium in ether-benzene solution.



Synthetic evidence is, however, generally regarded as inadmissible in such cases, unless, indeed, two valency isomerides are sufficiently stable to exist independently as, for example, is the case with *cyclobutene* and *butadiene*. It should be stated that the above synthesis is not regarded by its originator as a complete proof of the occurrence of the bridged phase of the nucleus.

A new benzene model has been suggested by Fraser,<sup>4</sup> but it does not appear to satisfy the necessary structural conditions. Briefly, it is the most symmetrical possible arrangement of six tetrahedra which will fulfil the requirements of the facts of isomerism of substituted derivatives and also bring the groups in the ortho-position into closer space relationship than those in the meta- and para-positions. The solution of this problem in geometry leads to a "twisted" Ladenburg prism formula in which each carbon atom is attached to two others in the *m*-positions and to the carbon atom

<sup>2</sup> R. Willstätter and J. Parnas, *Ber.*, 1907, **40**, 1406; R. Willstätter and F. Müller, *ibid.*, 1908, **41**, 2580.

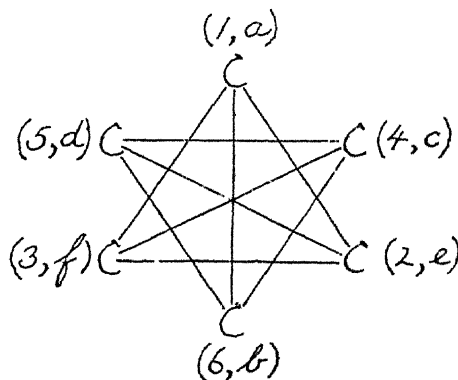
<sup>3</sup> C. K. Ingold, *T.*, 1922, **121**, 1143.

<sup>4</sup> R. Fraser, *ibid.*, 188.



in the *p*-position. It thus contains nine single bonds or, in the terminology of the octet theory, there are six octets connected by means of nine duplets. Adopting the hexagon convention in order to indicate the carbon atoms in *o*-, *m*-, and *p*-positions, the arrangement of valencies is as shown in the annexed figure, which closely resembles the stereographic projection of the model.

One of the chief of the many groups of facts which are at variance with this interpretation is concerned with the relations of aromatic and hydroaromatic compounds. Orientation in the benzene and *cyclohexane* series is in many cases an independent process and the results are always in agreement with the supposition that no serious rearrangement in the mode of linking of the carbon atoms occurs when a benzene derivative is reduced. In Fraser's model the unbroken *cyclohexane* rings are indicated by the figures 1, 2, 3, 4, 5, 6

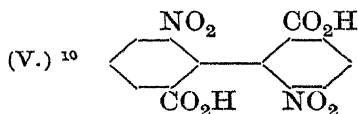


and letters *a*, *b*, *c*, *d*, *e*, *f*, and there may be other possibilities none of which represents the succession of atoms characteristic of the reduction products. Even in the formation of dihydro-derivatives it would be necessary to delete the nine bonds and replace them by entirely new ones and it is a severe strain on one's capacity for assimilation of new ideas. The tautomeric change of phloroglucinol into triketohexamethylene would similarly involve an alteration in position of each of the nine bonds. In terms of the prevailing version of the electronic theory of valency, the problem of the constitution of benzene becomes that of the disposition of eighteen electrons, twelve of which may be assumed to be involved in the formation of the ring. In regard to the remaining six, numerous suggestions have been made,<sup>5</sup> independently, but with points of

<sup>5</sup> H. Kauffmann, "Die Valenzlehre," p. 539; H. Stark, "Die Elektrizität in Chemischen Atom," p. 215; H. Pauly, *J. pr. Chem.*, 1918, [ii], 98, 118; W. O. Kermack and R. Robinson, *T.*, 1922, 121, 437; M. L. Huggins, *Science*, 1922, 55, 879; *A.*, i, 997; *J. Amer. Chem. Soc.*, 1922, 44, 1607; *A.*, i, 928; E. C. Crocker, *ibid.*, p. 1618; *A.*, i, 927.

contact especially in regard to the explanation of the laws of substitution. The further discussion of this highly speculative subject cannot be attempted here.

It will be recalled that, as the result of the X-ray analysis of crystals of naphthalene and other aromatic compounds, Sir William Bragg concluded that the characteristic hexagonal rings are puckered.<sup>6</sup> More recently, somewhat modified figures for the crystal molecules of benzene, naphthalene, and anthracene have been presented and are intended to show a solution which would be in agreement with the results so far obtained.<sup>7</sup> It is, at any rate, already clear that the carbon atoms in the individual crystal molecule do not lie in a plane. It is interesting to note that similar conclusions in regard to *cyclohexane* rings have been reached as the result of a study of the influence of stereoisomeric *cyclohexane*-diols on the conductivity of boric acid and of the behaviour of the glycols on condensation with acetone.<sup>8</sup> The chief obstacle to the acceptance of the view that this arrangement is a stable one, rather than a phase of an oscillation which may be suppressed in crystallisation or in the course of a reaction, lies in the fact that numerous cases of enantiomorphism should arise in substances hitherto regarded as composed of symmetrical molecules. Although its chief interest may possibly be in connexion with another matter, the opportunity may be taken to mention here the important achievement of the resolution of  $\gamma$ -6 : 6'-dinitrodiphenic acid (V) into optically active components.<sup>9</sup>



The resolution was carried out with the aid of brucine, and the acid from the less soluble salt had  $[\alpha]_D = +225^\circ$  and exhibited a tendency to racemise. The significant feature which distinguishes this example of enantiomorphism from all others is, of course, that the cause of the asymmetry must be sought in some property of the nucleus. The authors point out that their results may be explained on the basis of alternative hypotheses, and the one which is apparently favoured is that the two nuclei are not coplanar. In other words, Kaufler's diphenyl configuration or some modification

<sup>6</sup> Presidential Address to the Physical Society, *Proc. Phys. Soc.*, 1921, **34**, 33.

<sup>7</sup> Sir William Bragg, *T.*, 1922, **121**, 2783.

<sup>8</sup> H. G. Derx, *Rec. trav. chim.*, 1922, **41**, 312; *A.*, i, 651.

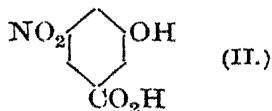
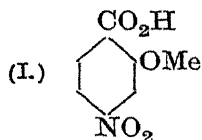
<sup>9</sup> G. H. Christie and J. Kenner, *T.*, 1922, **121**, 614.

<sup>10</sup> Compare *Ann. Reports*, 1921, p. 88.

of this is indicated. Indeed the support which Cain's work in the diphenyl series lent to Kaufler's view led to the prediction now verified, that certain members of the group might be resolvable.<sup>11</sup> If this explanation is accepted, and it appears reasonable from every point of view, it follows that the bond connecting the two phenyl nuclei is not in the plane of either of the benzene rings<sup>12</sup> and this is most easily understood on the basis of the benzene configuration deduced by Bragg. But it may be pointed out that the juxtaposition of two benzene rings in diphenyl and its derivatives is in some respects analogous to the packing of isolated molecules in the crystals and might conceivably have a similar effect in damping vibrations.

### Orientation.

The fact that *m*-nitrotoluene gives as one product of nitration 2 : 3 : 6-trinitrotoluene is of interest since, in this case, the nitroxyl enters every possible position *o*- and *p*- to the methyl group but apparently not at all *m*- to the nitro-group.<sup>13</sup> It is remarkable that *o*-methoxybenzoic acid should yield, on nitration, along with the normal products, no less than 27 per cent. of 4-nitro-2-methoxybenzoic acid (I),<sup>14</sup> because whilst *m*-directive groups are almost always also *o*-directive, it is very rarely that substitution in the *m*-position occurs with respect to a pronouncedly *o*-*p*-directive group. One of the very few instances on record may now be deleted from the literature, since it has been found that the acid obtained by Griess by the nitration of *m*-hydroxybenzoic acid and regarded by him as the 5-nitro-acid (II) is in reality 6-nitro-*m*-hydroxybenzoic acid and substitution occurs exclusively in the *o*- and *p*-positions with respect to hydroxyl. It is interesting that chlorination occurs in positions 2 and 6 but bromination leads only to the formation of 4-bromo-*m*-hydroxybenzoic acid.<sup>15</sup> In the nitration of nitroacetotoluidides, two instances have been recorded in which the presence or absence of sulphuric acid very greatly influences the position taken up by the entering substituent.



<sup>11</sup> H. King, *P.*, 1914, **30**, 250; J. F. Thorpe, *T.*, 1921, **119**, 535.

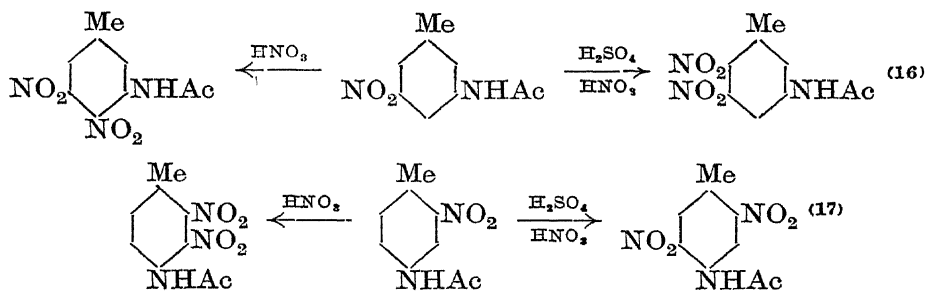
<sup>12</sup> J. Kenner, *Nature*, 1922, **109**, 581; *A.*, i, 533.

<sup>13</sup> O. L. Brady, *T.*, 1922, **121**, 328.

<sup>14</sup> V. Froelicher and J. B. Cohen, *ibid.*, 1652.

<sup>15</sup> P. H. Beyer, *Rec. trav. chim.*, 1921, **40**, 621; *A.*, i, 37.

In the following scheme, the main products are indicated.



In sulphonation of naphthols and naphthylamines the apparently perplexing results can readily be collated with the orientation rules developed in the benzene series if certain of the peculiarities of naphthalene, such as the reactivity of hydrogen atoms in the  $\alpha$ -positions, are taken into account. Thus, by analogy with phenol, the points of attack in  $\beta$ -naphthol should be positions 1, 3, 6, and 8, and these are the positions occupied by sulphonic radicles in the well-known, technically useful acids prepared by direct sulphonation. It is now shown that bromination of  $\beta$ -naphthol leads to the 1-, 1 : 6-, 1 : 3 : 6-, and 1 : 3 : 4 : 6-bromo-derivatives.<sup>18</sup> The formation of the last substance involves attack of position 4, which is *m*- to hydroxyl, but it is also *o-p*- to bromine, so that the result is not surprising.

#### *Reactions and Preparative Methods.*

*Reduction.*—Stereoisomeric cyclohexanetriols are obtained from each of the three trihydroxybenzenes by catalytic reduction in aqueous or alcoholic solution at 140° under pressure. The catalyst used is nickel.<sup>19</sup> The usefulness of Rosenmund's process for the preparation of aldehydes by catalytic reduction of acid chlorides is well illustrated by the preparation of gallaldehyde in quantity by way of its triacetate,<sup>20</sup> and the method has also been successfully applied to a number of chlorides of dibasic acids, for example, isophthalyl and terephthalyl chlorides.<sup>21</sup> The reduction of nitrobenzene in neutral media by means of hydrogen in presence of

<sup>16</sup> O. L. Brady, J. N. E. Day, and W. J. W. Rolt, *T.*, 1922, **121**, 526.

<sup>17</sup> J. Scott and R. Robinson, *ibid.*, 844.

<sup>18</sup> H. Franzen and G. Stäuble, *J. pr. Chem.*, 1921, [ii], **103**, 352; *A.*, i, 450.

<sup>19</sup> J. B. Senderens and J. Aboulenc, *Compt. rend.*, 1922, **174**, 616; *A.*, i, 337.

<sup>20</sup> K. W. Rosenmund and E. Pfannkuch, *Ber.*, 1922, **55**, [B], 2357; *A.*, i, 1030.

<sup>21</sup> K. W. Rosenmund, F. Zetzsche, and C. Flüttsch, *ibid.*, 1921, **54**, [B], 2888; *A.*, i, 39.

palladised animal charcoal at the ordinary temperature leads to the production of  $\beta$ -phenylhydroxylamine in a yield of 80 per cent.<sup>22</sup>

Ammonium sulphite has been recommended as a reducing agent applicable to the preparation of arylhydrazines, particularly those containing nitro-groups, from related diazonium salts.<sup>23</sup>

*Nitration.*—Quite a novel nitrating agent has been found in anhydrous pyridinium nitrate, applied in presence of excess of pyridine. Naphthalene yields  $\alpha$ -nitronaphthalene (40 per cent.), and anthracene yields 9-nitroanthracene (70 per cent.), when treated in this manner.<sup>24</sup> The nitration of quinol dibenzoate never yields a mononitro-derivative but instead 2 : 6-dinitroquinol dinitrobenzoate. When, however, 2-nitroquinol dibenzoate was obtained by another process, it was found to be impossible to introduce a second nitroxyl into the quinol nucleus. This interesting observation can only be explained by the abnormal reactivity of a molecule at the moment of its formation.<sup>25</sup>

*Halogenation.*—A very powerful chlorinating agent is produced in a mixture of sulphur monochloride and sulphuryl chloride by the addition of anhydrous aluminium chloride and appears to be an aluminium sulphur chloride of the composition,  $\text{Al}_2\text{S}_2\text{Cl}_8$ . In conjunction with sulphuryl chloride, this substance readily changes chlorobenzene into dichlorobenzenes, tetrachlorobenzene, and hexachlorobenzene in successive stages.<sup>26</sup> An investigation of the products formed by the chlorination of benzoyl chloride in presence of anhydrous ferric chloride has shown that the percentages of the isomerides obtained are *o*- 14.5, *m*- 83.5, *p*- 2.0, and details are given of the preparation of pure *m*-chlorobenzoic acid by this method.<sup>27</sup> Important advances from the preparative point of view have also resulted from a research on the chlorination of the three toluoyl chlorides at temperatures varying from 160—240°.<sup>28</sup> In this case, substitution naturally occurs in the methyl group and substances of the types



are obtained in good yield. The *o*-, *m*-, and *p*-w-dichlorotoluoyl

<sup>22</sup> K. Brand and J. Steiner, *Ber.*, 1922, **55**, [B], 875; *A.*, i, 536.

<sup>23</sup> W. Davies, *T.*, 1922, **121**, 715.

<sup>24</sup> M. Battegay and Ph. Brandt, *Bull. Soc. chim.*, 1922, [iv], **31**, 910; *A.*, i, 1001.

<sup>25</sup> F. Kehrman, M. Sandoz, and R. Monnier, *Helv. Chim. Acta*, 1921, **4**, 941; *A.*, i, 33.

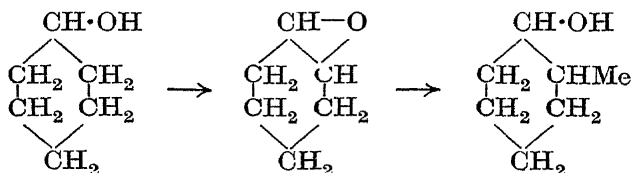
<sup>26</sup> O. Silberrad, *T.*, 1922, **121**, 1015.

<sup>27</sup> E. Hope and G. C. Riley, *ibid.*, 2510.

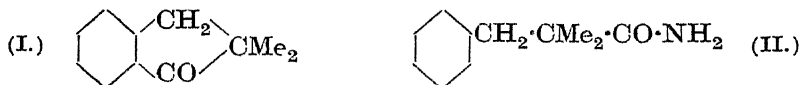
<sup>28</sup> W. Davies and W. H. Perkin, *ibid.*, 2202.

chlorides on digestion with milk of lime or chalk in an inert atmosphere yield the three phthalaldehydic acids in a pure condition, and this is the simplest method of preparation of these valuable substances. Somewhat unexpectedly it was found possible to hydrolyse the three  $\omega$ -trichlorotoluoyl chlorides by careful treatment with formic acid and so to obtain the *o*-, *m*-, and *p*-trichlorotoluic acids,  $\text{CCl}_3\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , which are relatively stable, crystalline substances.

*Alkylation.*—*cyclo*Hexanol may be converted into a stereoisomeride of the known 2-methyl*cyclo*hexanol (obtained by catalytic reduction of *o*-cresol) by conversion into *cyclo*hexene, oxidation of the latter by means of perbenzoic acid in chloroform solution with production of the *oxide*, and finally by the action of magnesium methyl iodide on this substance.<sup>29</sup>



Another ingenious alkylation process is illustrated by the preparation of  $\beta$ -phenyl- $\alpha\alpha$ -dimethylpropionic acid from  $\beta$ -phenylpropionic acid. This substance is first converted into  $\alpha$ -hydrindone by Kipping's method, and the ketone alkylated by means of sodamide and methyl iodide. The product is 2:2-dimethylindan-1-one (I) and this may be decomposed by sodamide with formation of the amide of the desired acid (II).



The process is rendered more generally applicable to an acid  $\text{R}'\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  by the stages  $\text{R}'\cdot\text{CH}_2\cdot\text{COCl}$ ,  $\text{R}'\cdot\text{CH}_2\cdot\text{COPh}$ ,  $\text{R}'\cdot\text{CR}_2\cdot\text{COPh}$ ,  $\text{R}'\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}_2$ .<sup>30</sup> On heating ethylene chlorohydrin with toluene-*p*-sulphonyl chloride,  $\beta$ -chloroethyl toluene-*p*-sulphonate,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , is obtained in a yield of more than 90 per cent. This ester is a valuable agent for the introduction of the chloroethyl group into phenols and amines. The method is far more convenient and gives much better yields than those depending on the use of ethylene halides.<sup>31</sup>

*Condensations.*—The use of sulphoacetic acid, prepared by

<sup>29</sup> M. Godchot and P. Bédos, *Compt. rend.*, 1922, **174**, 461; *A.*, i, 334.

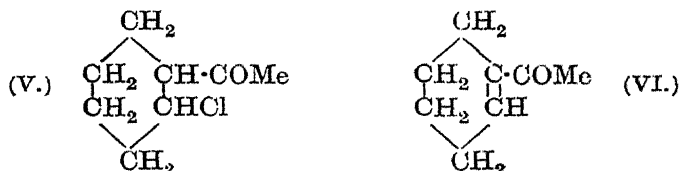
<sup>30</sup> A. Haller and E. Bauer, *Ann. Chim.*, 1921, [ix], **16**, 340; *A.*, i, 258.

<sup>31</sup> G. R. Clemons and W. H. Perkin, *T.*, 1922, **121**, 642.

mixing acetic anhydride and sulphuric acid, as a synthetical agent continues to give results of interest. Under specified conditions, guaiacol may be converted by this reagent into acetylisoacetovanillone (III),<sup>32</sup> whilst pyrogallol 1 : 3-dimethyl ether is acetylated in the nucleus even when it is heated with acetic anhydride and a few drops of sulphuric acid. In this case, the product is 3-acetoxy-2 : 4-dimethoxyacetophenone (IV).<sup>33</sup>



It is generally believed that the mechanism of substitution in the aromatic series comprises two main stages; an addition and then a fission of the additive product. The second reaction is, however, usually so rapid that the initial phases of the process are difficult to recognise, although this is not invariably the case. In the olefine series, the addition is more facile and the fission more difficult than in the aromatic series. Advantage has been taken of this circumstance in connexion with some experiments on the mechanism of the Friedel-Crafts' reaction. It has been shown that, under the influence of aluminium chloride, acetyl chloride unites with *cyclohexene* with the production of 2-chlorocyclohexyl methyl ketone (V), which is isolable and convertible by the further action of aluminium chloride in carbon disulphide solution into tetrahydroacetophenone (VI).<sup>34</sup>



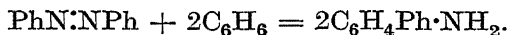
The function of the aluminium chloride is identical in both stages and is considered to be concerned with the weakening of the link between carbon and chlorine. A peculiar application of the catalytic activity of aluminium chloride is the elimination of hydrogen from aromatic nuclei. This is always effected in presence of nitrobenzene, which exercises a specific influence. The best known examples are the syntheses of complex polynuclear compounds due to Scholl and his collaborators, for example, that of pyranthrone

<sup>32</sup> W. Schneider and E. Kraft, *Ber.*, 1922, **55**, [B], 1892; *A.*, i, 750.

<sup>33</sup> K. Brand and H. Collischön, *J. pr. Chem.*, 1921, [ii], **103**, 329; *A.*, i, 452.

<sup>34</sup> H. Wieland and L. Bettag, *Ber.*, 1922, **55**, [B], 2246; *A.*, i, 1033.

from dibenzoylpyrene by intramolecular condensation. The reaction is capricious in its vagaries, but has now been applied to certain simple compounds. Thus benzil yields phenanthraquinone (25 per cent.) and  $\alpha$ -naphthyl ethyl ether yields 4:4'-diethoxy-1:1'-dinaphthyl (70 per cent.).<sup>35</sup> Attempts have been made to replace the nitrobenzene by azobenzene, but this is not possible in most cases. Aminodiphenyl is obtained, however, in a yield of 70—80 per cent. by the regulated action of aluminium chloride at 60° on a mixture of benzene and azobenzene.<sup>36</sup> The explanation advanced includes four stages, which are summed up in the equation



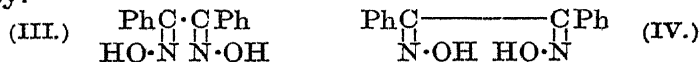
On account of the excellent yields and the relation of the products to naturally occurring compounds the synthesis of  $\beta$ -keto-bases from ketones, formaldehyde, and amine salts is noteworthy. A typical instance is afforded by the preparation of  $\omega$ -dimethylaminopropiophenone, obtained as its hydrochloride by heating together equivalent quantities of acetophenone, paraformaldehyde, and dimethylamine hydrochloride in concentrated alcoholic solution:  $\text{COPhMe} + \text{CH}_2\text{O} + \text{NHMe}_2 \rightarrow \text{COPh.CH}_2\text{CH}_2\text{NMe}_2$ .<sup>37</sup>

#### Molecular Rearrangements.

Admittedly the allocation of specific configurations to stereoisomeric oximes rests on a slender foundation, and one of the sign-posts has, it now appears, been turned in the wrong direction. The unwarranted assumption that in the Beckmann change groups in a *cis*-position are transposed has been proved to be erroneous by J. Meisenheimer.<sup>38</sup> 3:4:5-Triphenylisooxazole (I) is oxidised by chromic acid, or by ozone, with formation of benzoyl- $\beta$ -benzilmonoxime (II).



This independent and probably trustworthy determination of configuration involves the alteration of the formulæ, at present accepted, of the dioximes of benzil; the  $\alpha$ -dioxime is III and the  $\beta$ -modification is IV, no change being required in regard to the  $\gamma$ -variety.



<sup>35</sup> R. Scholl and G. Schwarzer, *Ber.*, 1222, 55, [B], 324; *A.*, i, 331; R. Scholl and C. Seer, *ibid.*, 330; *A.*, i, 336.

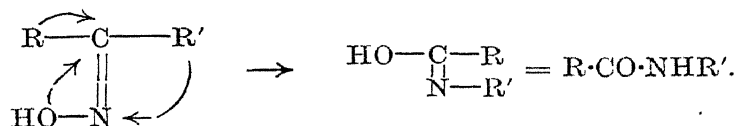
<sup>36</sup> R. Pummerer and J. Binapfl, *ibid.*, 1921, 54, [B], 2768; *A.*, i, 24.

<sup>37</sup> C. Mannich and G. Heilner, *ibid.*, 1922, 55, [B], 356; *A.*, i, 351; C. Mannich and D. Lammering, *ibid.*, 3510.

<sup>38</sup> *Ibid.*, 1921, 54, [B], 3206; *A.*, i, 152.



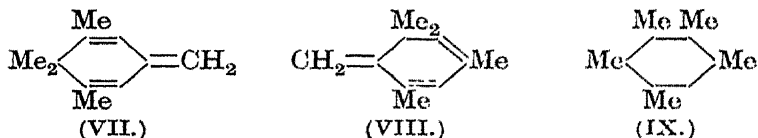
These corrections should be noted by writers of text-books and constitute an excellent example of the prudence of employing non-committal prefixes to distinguish stereoisomerides. The Beckmann transformation must now be represented as occurring in accordance with the scheme :



In continuance of earlier work, a comparative study has been made of the "semibenzene" hydrocarbons and their aromatic isomerides.<sup>39</sup> The semibenzenes have the lower densities and the higher molecular refractions and dispersions. The simplest member of the series is 1:1-dimethyl-4-methylene- $\Delta^{2,5}$ -cyclohexadiene (V), which passes very readily into  $\psi$ -cumene (VI), with development of heat, when a drop of hydrochloric acid is added to its solution in acetic acid.



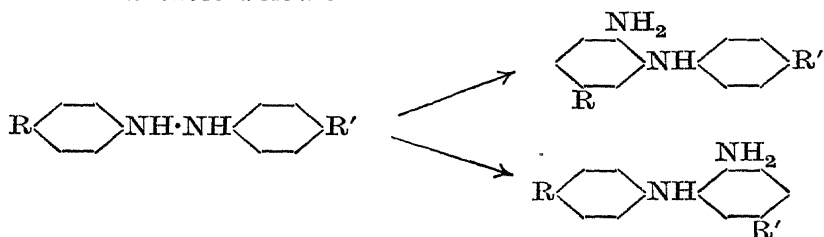
This transfer of the alkyl group to the adjacent carbon atom represents the normal occurrence, but instances of migration to the meta-position are not lacking. Thus the semibenzene VII is changed by warming with a mixture of acetic and sulphuric acids into pentamethylbenzene (IX). The possibility might be queried that this is a double migration through the intermediate stage VIII or a related hydrated compound.



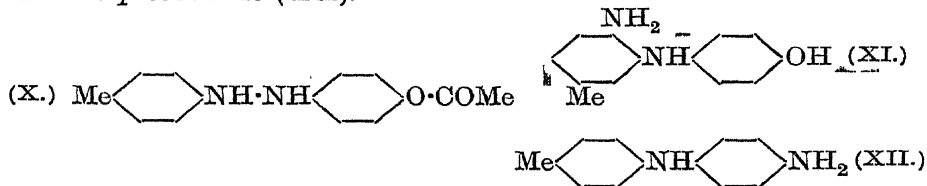
In the transformation of methylaniline hydrochloride into *p*-toluidine hydrochloride the main factor is found to be the temperature employed, and the course of the change is but little affected by the addition of salts such as zinc chloride or aluminium chloride. At 310°, there is notable production of dimethylaniline, and this tends to confirm the view that the migration is due to successive reactions, the methylaniline hydrochloride decomposing into aniline and methyl chloride, which react with formation of the original substances (reversible), of dimethylaniline (reversible), and of

<sup>39</sup> K. von Auwers and K. Ziegler, *Annalen*, 1921, **425**, 217; *A.*, i, 119.

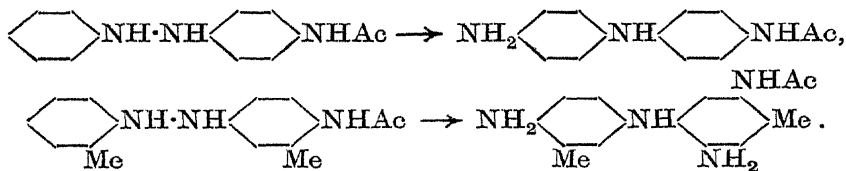
*p*-toluidine (irreversible).<sup>40</sup> A long paper<sup>41</sup> has been published by P. Jacobsen describing further developments of his exhaustive investigations of the isomeric changes of hydrazo-compounds. On the whole, the results resemble those with which we are already familiar, but the following points may be mentioned. If an ortho-position is free, di-*p*-substituted hydrazobenzenes yield *o*-semidines which, in case the substituents are different, have one of two formulæ as indicated below :



In no instance were both possible *o*-semidines isolated. If the convention is adopted that the amino-group of the semidine occurs in the *p*-position to that one of the two *p*-substituents in the hydrazo-compound which has the greater "directing power" in the transformation, then, of all the groups examined, ethoxyl is the most powerful and methyl comes next in order. When R is acetoxy, a *p*-semidine is formed by displacement of the group; thus 4'-acetoxy-4-methylhydrazobenzene (X) yields the *o*-semidine (XI) and the *p*-semidine (XII).



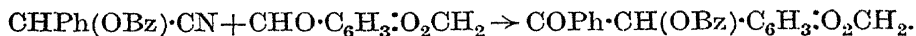
This extrusion of oxygen, directly united to the aromatic nucleus, is a very rare phenomenon. No example of the *o*-benzidine change was encountered in the benzene series, but its occurrence in the naphthalene group was confirmed. The following comparison is interesting :



<sup>40</sup> E. Beckmann and E. Correns, *Ber.*, 1922, 55, [B], 852; *A.*, i, 535.

<sup>41</sup> *Annalen*, 1922, 427, 142; *A.*, i, 589.

In the second case figured, the *p*-semidine is also formed but in very small relative amount. Migration of a benzoyl group is proved to occur in the course of the synthesis of benzoylmethylenedioxybenzoin by the action of an alcoholic solution of sodium ethoxide on a mixture of benzoylmandelonitrile and piperonal : <sup>42</sup>



This confirms Lapworth's theory that the production of benzoin in the usual manner depends fundamentally on the aldol-like condensation of benzaldehyde and mandelonitrile.

### *Reactivity of Halogen Atoms in Carbon Compounds.*

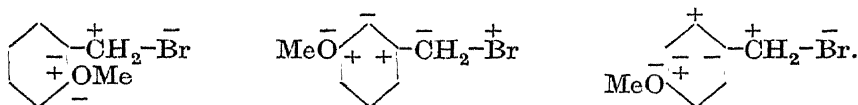
The reactivity of halogen is of two main types which may coexist but are exhibited to an unequal degree in any one compound. The atom is in some cases readily replaced by such groups as —OH, NH<sub>2</sub>, and in other instances it is essentially reducible and oxidising. The extreme hydrolysable type is represented by chlorine in the acid chlorides. This, it should be noted, is also reducible under the correct conditions, but the reaction is far from being as characteristic as that of replacement by hydroxyl. The reducible type is found in the hypochlorites, in substances containing the group —NCl— such as the *N*-chlorosulphonamides, and in  $\alpha\alpha$ -dihalogenated  $\beta$ -diketones. In these cases replacement of the halogen by hydroxyl is still possible, but is often a very difficult operation. Adherents of the various brands of polarity theories speak of the halogen as negative or positive and this is at least a useful classification of a wide range of phenomena. It is perhaps a little more accurate and certainly more non-committal to regard the atom to which the halogen is attached as positive and negative respectively. A very interesting series of observations has been made on the influence of substituents in the benzene ring on the mobility of chlorine in the shortest side chain.<sup>43</sup> The reaction measured was the hydrolysis of the various benzyl chlorides and the influence of the groups was found to be in the order : *p*-Me > *o*-Me > *m*-Me > H > *p*-Cl > *o*-Cl > *m*-Cl > *m*-NO<sub>2</sub> > *o*-NO<sub>2</sub> > *p*-NO<sub>2</sub>.

Now the groups Me, H, Cl, NO<sub>2</sub> represent a descending series in regard to the electropositive character of the constituent atoms and the results show that, independent of the position of the substituent, the more electropositive is the molecule the quicker is the hydrolysis. This is an example of the *general polar* effect, the direction of which is explained by the consideration that the reaction is fundamentally, under the conditions employed, an attack on the molecule by

<sup>42</sup> H. Greene and R. Robinson, *T.*, 1922, **121**, 2182.

<sup>43</sup> S. C. J. Olivier, *Rec. trav. chim.*, 1922, **41**, 301; *A.*, i, 646.

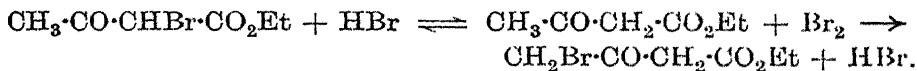
negative hydroxyl ions. In a similar investigation of the speed of synthesis of sulphones by the condensation of benzene with substituted benzenesulphonyl chlorides, the series was expanded to :  $\text{Me} > \text{H} > \text{I} > \text{Br} > \text{Cl} > \text{NO}_2$ . But on comparing the effect of position of the substituent on the reactivity, it will be seen that  $-\text{CH}_3$  and  $\text{Cl}-$  exercise their greatest influence from the *p*- and *o*-positions, whilst *m*- $\text{NO}_2$ -benzyl chloride is more reactive than its isomerides. This reversal in passing from groups which are negative on the basis of the theory of *alternating* polarity, to a group which, on the same grounds, must be considered positive is in agreement with the work of Lapworth and Shoesmith (see below) and the whole research throws some light on the relative importance to be attached to the general and alternate polar effects. If the methoxy-compounds had been included in the series, there is little doubt that *o*- and especially *p*-methoxybenzyl chloride would have proved the most reactive of the substances investigated. This is to be expected because there is strong evidence that methoxyl is conjugated with the nucleus, a circumstance which allows the alternate effect to overpower the general effect and throws such groups as methoxyl and amino out of their natural order. If the correlation of the two types of reactivity of halogen with polarity effects is well founded, then it must follow that positional influences which facilitate hydrolysis of alkyl or aryl halides will render reduction more difficult and vice versa. Again, the general effect must be eliminated by comparing isomerides only. Such a comparison has been made of the three methoxybenzyl bromides and the results are in excellent agreement with the theory.<sup>44</sup> The effect of the negative methoxyl group on the bromine atom is illustrated in the following expressions, in which the signs have a purely relative significance :



It will be seen that in the *o*- and *p*-compounds the result is to enhance the natural polarity of the bromine, whereas the reverse is the case in *m*-methoxybenzyl bromide. Therefore *o*- and *p*-methoxybenzyl bromides should be more readily hydrolysed than the *m*-isomeride, and this was found to be the case to a very striking extent. Numerous examples of the high reactivity of bromine in a side chain *p*- to methoxyl were, however, already known and the second part of the prediction, that the *m*-methoxybenzyl bromide

<sup>44</sup> A. Lapworth and J. B. Shoesmith, *T.*, 1922, 121, 1391.

should be found to contain the more reducible halogen, is therefore all the more valuable as a test of the hypothesis because it could not have been made by analogy with known reactions and without considerations based on induced polarities. Experiments on the reduction of the methoxybenzyl bromides with hydrogen iodide showed that actually the *m*-derivative was the most readily attacked. This double verification of anticipated effects is not to be neglected in assessing the value of the theory in connexion with the problems of reactivity and mechanism of reactions. Halogen atoms in the *o*- or *p*-positions with respect to a strongly negative atom or group in the aromatic nucleus should evince positive polar character and this has already been shown by numerous investigators to be the case so far as reducibility is concerned. Additional evidence is supplied by the behaviour of certain iodinated benzene derivatives.<sup>45</sup> 3-Iodo-*p*-toluidine, *p*-iodoaniline, and 3-iodo-*p*-hydroxybenzoic acid are decomposed by boiling with 10 per cent. hydrochloric acid in such a way that the iodine is partly replaced by hydrogen and in compensation there is production of di- and tri-iodo-derivatives. Aceto-3-bromo-*p*-toluidide behaves in a similar manner. This substituting action in presence of acids is typical of the behaviour of positive halogen and is presumably due to elimination in the form  $\text{hal}^+(\text{OH})$ , as the result of the union of the negative carbon atom, or other atom to which the halogen is attached, with a hydrogen ion. Some significant examples have been previously recorded and perhaps the most interesting in the aromatic series is the formation of 3-bromo-2-aminoanthraquinone either by heating 1-bromo-2-aminoanthraquinone alone or a mixture of 2-aminoanthraquinone with 1 : 3-dibromo-2-aminoanthraquinone. The former reaction is the migration of bromine to a more stable position in the molecule and may be compared with the well-known change of ethyl  $\alpha$ -bromoacetoacetate into ethyl  $\gamma$ -bromoacetoacetate which occurs in presence of traces of hydrobromic acid.<sup>46</sup> The simplest explanation<sup>47</sup> takes cognisance of the highly positive character of the bromine atom in the  $\alpha$ -position, where it is under the influence of both the carbonyl and carbethoxyl groups, and involves the stages :



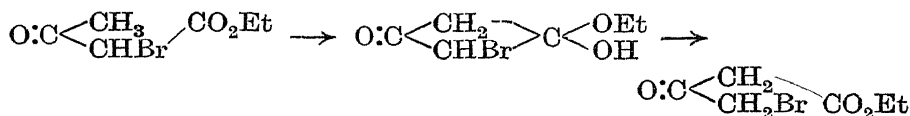
An alternative mechanism which has been suggested<sup>48</sup> is the following :

<sup>45</sup> B. H. Nicolet, *J. Amer. Chem. Soc.*, 1921, **43**, 2081; *A.*, i, 121.

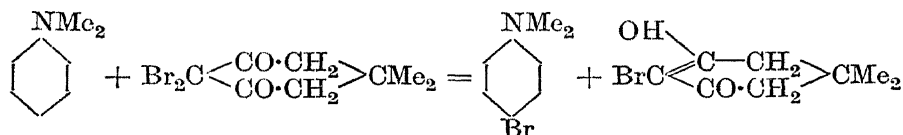
<sup>46</sup> A. Hantzsch, *Ber.*, 1894, **27**, 356, 3168; M. Conrad, *ibid.*, 1896, **29**, 1042.

<sup>47</sup> A. Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 8.

<sup>48</sup> G. T. Morgan and H. D. K. Drew, *T.*, 1922, **121**, 928.



This is untenable because in the similar rearrangement of ethyl  $\alpha$ -bromomethylacetoacetate,  $\text{CH}_3\cdot\text{CO}\cdot\text{CMeBr}\cdot\text{CO}_2\text{Et} \rightarrow \text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , the scheme involves transference of methyl as well as of bromine and the product should then have the constitution  $\text{CHBrMe}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , which does not appear to be the case.<sup>49</sup> There is no very cogent reason for supposing that substitutions by positive halogen must always depend on successive reactions and on the intervention of acids. Thus Wohl has shown that acetobromoamide is a useful brominating agent and he regards the reaction as occurring directly between the molecules concerned and involving the interchange of hydrogen and bromine.<sup>50</sup> On the other hand, an ingenious process of regulated chlorination by means of *N*-chloroacetanilide and hydrochloric acid in small but definite concentration is based on a directly contrary assumption.<sup>51</sup> The two views are not irreconcilable nor in any way contradictory and both are entertained by Orton in connexion with different migration phenomena. Thus the direct substitution is analogous to the transformation of phenylnitroamine into *o*-nitroaniline and the indirect to the conversion of the *N*-chloroacetanilides into the nuclear-substituted isomerides. In order to avoid the formation of hydrobromic acid in the course of bromination, it is now proposed<sup>52</sup> to employ dibromodimethyldihydroresorcinol as a brominating agent. This substance is reduced with uncommon ease and even by the action of dilute aqueous sodium hydroxide. It reacts quantitatively with dimethylaniline in the following sense :



As the enolic monobromo-derivative can be recovered and used again, the method may have practical value. Gupta and Thorpe do not adopt the view that the reactivity of the bromine exhibited in this reaction is due to its positive polar character, but prefer the hypothesis that the bromine is mobile because it inhibits a tautomeric process involving the keto-groups. There is a tendency to acquire

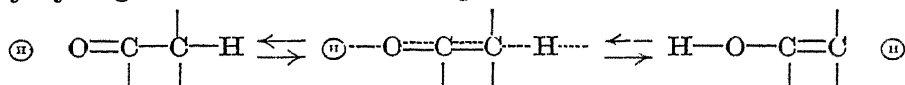
<sup>49</sup> M. Conrad and A. Kreichgauer, *Ber.*, 1896, **29**, 1042.

<sup>50</sup> *Ibid.*, 1919, **52**, [B], 51.

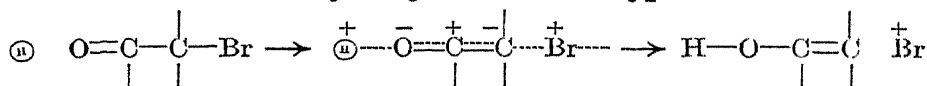
<sup>51</sup> K. J. P. Orton and H. King, *T.*, 1911, **99**, 1185.

<sup>52</sup> B. M. Gupta and J. F. Thorpe, *ibid.*, 1922, **121**, 1896.

a hydrogen atom necessary for tautomerism, and earlier examples of the application of this theory will be recalled. In the Reporter's opinion, both views are correct and are reconciled by the consideration that the system acquires its hydrogen atom by union of the latter with oxygen so that an enol is the first product. Thus the fundamental factor is the affinity of oxygen for hydrogen and few chemists will find it difficult to equate this with the negative electrochemical character of oxygen and the positive character of hydrogen. The hydrogen is probably acquired as a proton which attaches itself to the free electrons of the oxygen octets; the molecule thus becomes positively charged and recovers neutrality by reversing the process, acquiring an electron (potassiobenzophenone?) or as an important alternative by ejecting some other atom in a positively charged condition. In keto-enol tautomerism catalysed by hydrogen ions, we have the stages :



This may be compared with the following scheme in which the atom liberated is Br<sup>+</sup>, that is to say, bromine in a form which could combine with a hydroxyl ion to form hypobromous acid :



The tendency towards a more even distribution of valency is the driving force in the reaction and this is carried into effect by a process of conjugation, using that term in its wider meaning of re-distribution of affinity through a chain of atoms. On this interpretation it is seen that "the tendency to acquire a hydrogen atom necessary for tautomerism" is a phrase which accurately represents the phenomenon and is not at all inconsistent with the view that the bromine exhibits positive polarity. In any particular case of double decomposition, the actual charges mentioned above need not be acquired, because the interchange of hydrogen and bromine will be synchronous. Probably too, both oxygen atoms in the diketone attract the hydrogen and this can easily be represented with the aid of partial valencies. It should be emphasised that the alternate labelling of atoms in a chain with + and - signs is never intended to indicate the mechanism of the effect, which, as in the example under discussion, is often the result of conjugation. Further interesting substitution reactions due to positive halogen have been encountered in a study of the action of nitrogen trichloride on aromatic hydrocarbons.<sup>53</sup> Toluene is

<sup>53</sup> G. H. Coleman and W. A. Noyes, *J. Amer. Chem. Soc.*, 1921, **43**, 2211; *A.*, i, 133.

converted into benzyl chloride, monochlorotoluenes, and more highly chlorinated compounds. At the same time, some *N*-chloroaminotoluene derivatives are formed. Bromotrinitromethane contains a highly positive bromine atom and in aqueous hydrobromic acid solution is able to change phenol into its tribromo-derivative.<sup>54</sup> Reduction by titanous salts and oxidation of hydrazine with formation of nitrogen have been applied as tests for positive halogen, and an extensive comparative study of the effect of constitution on the property has been made.<sup>55</sup> The results are in very good agreement with the theory of induced alternate polarities of atoms in a chain, although some few details connected with degree of reactivity are not yet satisfactorily explained. This is not surprising, and it should be stated that, on account of the complexity of the factors which control the speed of reactions, the polarity theory cannot be successfully used to interpret relative reaction velocities except in carefully chosen cases. The chief necessary precautions are the avoidance of cases where the general polar effect and steric considerations are likely to be of importance and it is also desirable that the mechanism of the reaction should be known to a first approximation. One of the anomalous observations noted above is that dichloroacetylacetone,  $\text{COMe}\cdot\text{CCl}_2\cdot\text{COMe}$ , does not oxidise hydrazine under the specified conditions, whereas ethyl dichloromalonate,  $\text{CCl}_2(\text{CO}_2\text{Et})_2$ , readily does so. The explanation given is based on the larger number of key oxygen atoms in the latter substance, but this leads to inconsistencies, as pointed out by Gupta and Thorpe (*loc. cit.*), and indeed carbonyl is universally regarded as a more activating group than carbethoxyl.

#### *Triphenylmethyl and Related Subjects.*

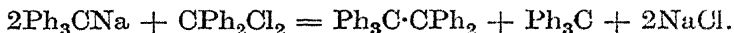
The electrical conductivity of solutions of triarylmethyl bromides in sulphur dioxide or hydrocyanic acid is comparable with that of aqueous solutions of potassium hydroxide and shows little variation among individuals. The molecular conductivities of the chlorides, however, are not so high and diphenyl- $\alpha$ -naphthylmethyl chloride is a better conductor than diphenyl- $\beta$ -naphthylmethyl chloride and this again than triphenylmethyl chloride. The order is that of the ease of dissociation of the corresponding hexa-arylethanes into the free radicles and also of the conductivity of the free radicles themselves. Diphenyl- $\beta$ -naphthylmethyl is obtained in the usual manner and the hexa-arylmethane, a pale yellow, crystalline powder,

<sup>54</sup> T. Henderson and A. K. Macbeth, *T.*, 1922, **121**, 892.

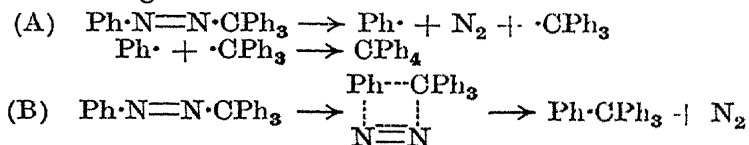
<sup>55</sup> Henderson and Macbeth, *loc. cit.*; E. L. Hirst and A. K. Macbeth, *T.*, 1922, **121**, 904, 2169; H. Graham and A. K. Macbeth, *ibid.*, 1109; A. K. Macbeth, *ibid.*, 1116.



m. p. 135—140°, is found by the cryoscopic method to be dissociated from 15 to 50 per cent. in eight solvents ranging in freezing point from -22° to +80°. The changes in colour of solutions of this substance due to alterations in concentration and temperature are by no means parallel to the changes in extent of dissociation. This shows that the equilibrium system is more complex than has often been assumed. It is suggested that in addition to dissociation there is also tautomerisation of the benzenoid radicle into a quinonoid modification.<sup>56</sup> It is perhaps well to note at this point that although to crystalline substances are now often given the names of the radicles produced in solution, the relation between the two states remains highly problematical. An interesting contribution to the subject is concerned with the preparation of pentaphenylethyl.<sup>57</sup> Sodium triphenylmethyl in ethereal solution is treated with benzophenone chloride, the containing vessel being filled with nitrogen. The products are pentaphenylethyl and triphenylmethyl and on concentration of the filtered liquid the former separates in coarse crystals and can be largely mechanically separated from the hexaphenylethane by swirling and decantation and completely by washing with ether.



Pentaphenylethyl forms golden-yellow crystals with a metallic glance and is almost entirely unimolecular in solution. Triphenylbiphenylene-ethyl,  $\text{Ph}_3\text{C}\cdot\overline{\text{C}_6\text{H}_4}\cdot\text{C}_6\text{H}_4$ , is similarly prepared from sodium triphenylmethyl and fluorenone chloride. It occurs in large, violet prisms and is wholly unimolecular in solution. The course of the decomposition of phenylazotriphenylmethane and of substituted derivatives has been examined with the object of determining whether free radicles are formed in the process or not.<sup>58</sup> Thus the production of tetraphenylmethane (Gomberg) might proceed according to the alternative schemes:



Actually it was found that triphenylmethyl was produced and could be recognised spectroscopically, by colour changes in hot and cold solution and by the formation of the peroxide. The phenyl radicle, presumably formed at the same time, combines with

<sup>56</sup> M. Gomberg and F. W. Sullivan, jun., *J. Amer. Chem. Soc.*, 1922, **44**, 1810; *A.*, i, 929.

<sup>57</sup> W. Schlenk and H. Mark, *Ber.*, 1922, **55**, [B], 2285, 2299; *A.*, i, 1002.

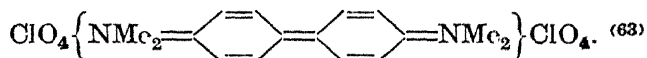
<sup>58</sup> H. Wieland, E. Popper, and H. Seefried, *ibid.*, 1816; *A.*, i, 772.

hydrogen, but the oxidised component thus necessitated has not yet been recognised. This proves beyond doubt that the azo-compound decomposes with formation of radicles, but it is not logically compulsory to proceed a further step and assume that the tetraphenylmethane formed owes its existence to the operation of scheme A rather than of scheme B. The application of the new method of preparation of triphenylmethyl to the radicles of the basic triphenylmethane dyes is of great interest. It was found, for instance, that phenylazobis-*p*-dimethylaminotriphenylmethane,  $\text{NPh}\cdot\text{N}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , yields on decomposition, benzene, nitrogen, and bis-*p*-dimethylaminotriphenylmethyl,  $\text{CPh}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , which is the radicle of malachite green. This unstable substance and tri-*p*-dimethylaminotriphenylmethyl,  $\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ , the radicle of crystal violet, are scarcely more coloured than triphenylmethyl itself. The observation is interpreted as supporting the quinonoid theory of the structure of the ions of the basic dyestuffs of the triphenylmethane group and it would certainly seem to exclude the Rosenstiehl formula, and Baeyer's ionisable bond modification of this, in a more definite way than has previously been possible. From the point of view of rational classification at least, the papers<sup>59</sup> which Hantzsch has published during the year bearing on the related subjects of the constitution of carbonium salts, halochromism, and solvatochromism, and on the theory of triphenylmethane derivatives contain much that is of value even though, as more than one author claims, many of his suggestions have been anticipated. The lamentable position into which organic chemistry threatens to drift is that there will be as many theoretical systems as theorists, and it is matter for congratulation when several chemists independently arrive at somewhat similar conclusions. It would be impossible to give an adequate exposition of Hantzsch's system in this place, but it may be well to refer to one matter. Only two types of triphenylmethane derivatives are recognised, the colourless non-conducting variety and the coloured conducting, true carbonium compounds in which carbon has normally the co-ordination number 3. Both types are present in the equilibrated system:  $\text{Br}\cdot\text{CPh}_3 \rightleftharpoons [\text{CPh}_3]\text{Br}$ , which may be shifted to the right by the introduction of substances which readily form complex anions with the bromine. But, on the other hand, triphenylmethyl may also function as an anion in such substances as  $\text{Na}[\text{CPh}_3]$ , which are also coloured.

This conception of triphenylmethyl as an amphoteric ion leads naturally to the suspicion that the coloured hexa-arylethanes are also complex compounds having the formula  $[\text{Ar}_3\text{C}][\text{Ar}_3\text{C}]$ .

<sup>59</sup> A. Hantzsch, *Ber.*, 1921, 54, [B], 2573, 2613, 2620, 2627; 1922, 55, [B], 953; *A.*, i, 24—26, 556. Compare also *A.*, i, 331, 445.

Carbinols containing phenylethynyl groups have been prepared and found to exhibit typical halochromism.<sup>60</sup> For example, triphenylethynylcarbinol,  $(\text{CPh:C})_3\text{C}\cdot\text{OH}$ , is obtained by the action of magnesium phenylethynyl bromide on phenylpropiolyl chloride. It gives a bluish-violet coloration with sulphuric acid, deep bluish-violet with perchloric acid, and bright blue with stannic chloride. The conclusion drawn is that the halochromy of triphenylcarbinols is not to be associated with changes in the benzene rings, since the typical phenomena can be reproduced when "gap linkings" are introduced between the carbinol group and the nuclei. A number of distinct investigations published during the year bear on the same subject.<sup>61</sup> Diphenylphenylethynylcarbinol is converted by acetyl chloride, acetic anhydride, and the like and by hydrogen chloride in ethereal solution into phenyl  $\alpha$ -phenylstyryl ketone: <sup>62</sup>  $\text{CPh:C}\cdot\text{CPh}_2\cdot\text{OH} \rightarrow \text{COPh}\cdot\text{CH:CPh}_2$ . That the arrangement of carbon atoms remains undisturbed (wandering of phenyl was a possibility) was proved by carrying out the transformation:  $\text{CPh:C}\cdot\text{C}(\text{C}_6\text{H}_4\text{Cl})_2\cdot\text{OH} \rightarrow \text{COPh}\cdot\text{CH:C}(\text{C}_6\text{H}_4\text{Cl})_2$  and oxidising the product to *pp'*-dichlorobenzophenone. The puzzling feature of the reaction is that it occurs so readily in the absence of water. It may be mentioned here that the fate of over-oxidised leuco-bases of the triphenylmethane dyestuffs has been ascertained. The gradual treatment at the ordinary temperature of a moderately concentrated malachite-green solution, acidified with sulphuric acid, with lead peroxide until a diluted sample shows no green tinge, followed by filtration and addition of perchloric acid, precipitates orange needles of tetramethyldiphenoneimonium perchlorate,



The same perchlorate results from the oxidation of tetramethylbenzidine or of Michler's hydrol.

#### *Alicyclic Group.*

There is much overlapping of the subject matter of the sections of this report and numerous references to alicyclic compounds will be found elsewhere. A synthesis of 1-methylcyclopropane-1-carboxylic acid (I) has been carried through the following

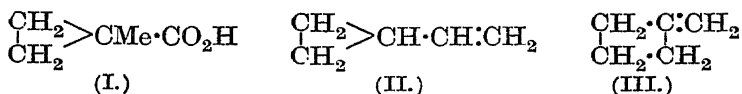
<sup>60</sup> K. Hess and W. Weltzien, *Ber.*, 1921, **54**, [B], 2511; *A.*, i, 35.

<sup>61</sup> F. Straus and A. Dützmann, *J. pr. Chem.*, 1921, [ii], **103**, 1; *A.*, i, 148; K. Ziegler, *Ber.*, 1921, **54**, [B], 3003; *A.*, i, 151; S. Skraup and L. Freundlich, *ibid.*, 1922, **55**, [B], 1073; *A.*, i, 539; K. H. Meyer and K. Schuster, *ibid.*, 815; *A.*, i, 540.

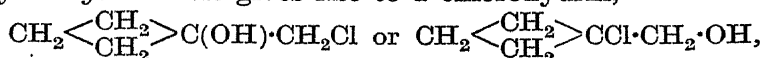
<sup>62</sup> *Ibid.*, 819; *A.*, i, 556.

<sup>63</sup> F. Kehrman, G. Roy, and (Miss) M. Ramm, *Helv. Chim. Acta*, 1922, **5**, 153; *A.*, i, 467.

stages : <sup>64</sup> Formaldehyde (2 mols.) and propaldehyde (1 mol.) are condensed to dihydroxy- $\alpha\alpha$ -dimethylpropaldehyde,  $\text{CHO}\cdot\text{CMe}(\text{CH}_2\cdot\text{OH})_2$ , which is converted into its *oxime* and then by the action of acetic anhydride into diacetoxypivalonitrile. The latter, by heating with saturated hydrobromic acid at  $125\text{--}130^\circ$  during twenty hours, yields dibromopivalic acid,  $\text{CMe}(\text{CH}_2\text{Br})_2\cdot\text{CO}_2\text{H}$ . Methyl dibromopivalate reacts with zinc dust in methyl alcoholic solution with formation of methyl 1-methylcyclopropane-1-carboxylate.



The isomeric hydrocarbons vinylcyclopropane (II) and methylenecyclobutane (III) have each been produced by the decomposition of suitable quaternary ammonium compounds.<sup>65</sup> Acetylcyclopropan-oxime,  $\begin{array}{c} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \end{array} > \text{CH}\cdot\text{CMe}\cdot\text{NOH}$ , is reduced to the amine, which is fully methylated and the iodide converted to hydroxide. The distillation of this trimethyl- $\alpha$ -cyclopropylethylammonium hydroxide,  $\begin{array}{c} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \end{array} > \text{CH}\cdot\text{CHMe}\cdot\text{NMe}_3\}\text{OH}$ , furnishes chiefly vinylcyclopropane and very little of the tertiary base. Methylenecyclobutane is similarly prepared in small yield from cyclobutylmethyltrimethylammonium hydroxide,  $\text{CH}_2\langle\begin{array}{c} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \end{array}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{NMe}_3\}\text{OH}$ , which, however, gives on decomposition cyclobutylmethyldimethylamine as the main product. The action of hypochlorous acid on methylenecyclobutane gives rise to a chlorohydrin,



the former being indicated by analogies. This is converted into cyclopentanone when it is heated with litharge and water, whilst the action of aqueous potassium hydroxide produces an oxide,  $\text{CH}_2\langle\begin{array}{c} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \end{array}\rangle\text{C}\langle\begin{array}{c} \text{CH}_2 \\ | \\ \text{O} \end{array}\rangle$ , which may be isomerised to cyclobutane-aldehyde,  $\text{CH}_2\langle\begin{array}{c} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \end{array}\rangle\text{CH}\cdot\text{CHO}$ , by the action of zinc chloride.<sup>66</sup>

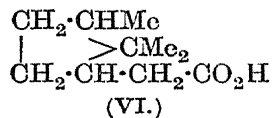
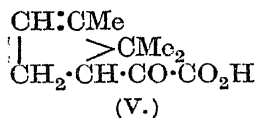
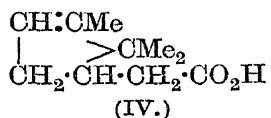
When campholenic acid (IV) is treated with an aqueous solution of calcium hydroxide and with silver oxide at  $60^\circ$ , it is partly reduced to camphor and partly oxidised to  $\alpha$ -ketocampholenic acid (V).<sup>67</sup>

<sup>64</sup> M. Kohn and A. Mendelewitsch, *Monatsh.*, 1921, **42**, 227; *A.*, i, 518.

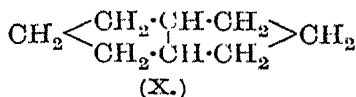
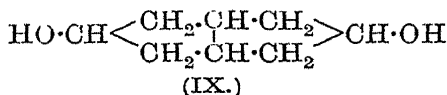
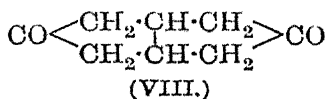
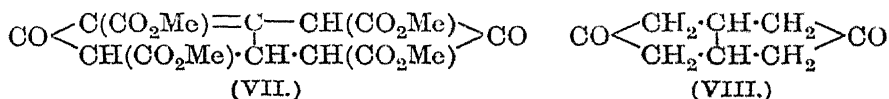
<sup>65</sup> N. J. Demjanov and (Miss) M. Dojarenko, *Ber.*, 1922, **55**, [B], 2718, 2727; *A.*, i, 1014, 996.

<sup>66</sup> *Ibid.*, 2730; *A.*, i, 1009.

<sup>67</sup> J. P. C. Chandrasena and C. K. Ingold, *T.*, 1922, **121**, 1552.

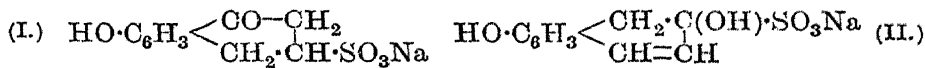


The yield of camphor obtained is stated to be small, but is not precisely specified, so that it is difficult to form an independent opinion as to the significance of this very striking observation. If the view put forward, that *trans*-dihydrocampholenic acid (VI) is the intermediate stage, is correct, then we have another and a peculiar instance of the abnormal reactivity of a newly formed molecule, because both *cis*- and *trans*-dihydrocampholenic acids have been isolated by another investigator in their racemic forms and found to be perfectly stable substances.<sup>68</sup> The condensation of chloral with methyl malonate leads to the formation of methyl 0 : 3 : 3-*dicyclo*- $\Delta^1$ -octene-3 : 7-dione-2 : 4 : 6 : 8-tetracarboxylate (VII), which can be converted by hydrolysis and reduction into the diketone (VIII), the glycol (IX), and finally into 0 : 3 : 3-*dicyclo*-octane (X).<sup>69</sup>



#### Tautomerism.

1 : 5-Dihydroxynaphthalene reacts with sodium hydrogen sulphite to produce a compound,  $\text{C}_{10}\text{H}_{10}\text{O}_8\text{S}_2\text{Na}_2$ , which, on boiling with water, loses one molecular proportion of sodium hydrogen sulphite and is changed to sodium 5-hydroxy-1-ketotetrahydronaphthalene-3-sulphonate (I). 2 : 7-Dihydroxynaphthalene behaves somewhat differently and gives the compound II, which is converted by dry ammonia at  $100^\circ$  into a corresponding amino-derivative (III). The latter on decomposition with water yields 7-amino-2-naphthol.<sup>70</sup>

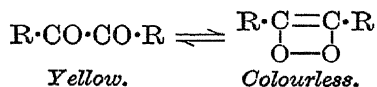


<sup>68</sup> P. Lipp, *Ber.*, 1922, 55, [B], 1883; *A.*, i, 735.

<sup>69</sup> G. Schroeter and G. Vossen, *Annalen*, 1922, 426, 1; *A.*, i, 122.

<sup>70</sup> W. Fuchs and W. Stix, *Ber.*, 1922, 55, [B], 658; *A.*, i, 451.

The series of reactions throws light on the mechanism of Bucherer's process for the conversion of naphthols into naphthylamines, but it is surprising that it should also be claimed as a demonstration of the tautomerism of the dihydroxynaphthalenes. It has long been thought that the  $\alpha$ -diketones may exist in a peroxide form, and Willstätter's discovery of colourless and coloured modifications of *o*-benzoquinone was interpreted in this way. Definite confirmation of the accuracy of the hypothesis is now provided by a careful investigation of the benzils.<sup>71</sup> Normally, these compounds are, of course, yellow, but in certain cases they have been found to be colourless or almost so. The first example was discovered by J. C. Irvine in 1907 when he prepared the colourless 2 : 2'-dimethoxybenzil.<sup>72</sup> The coloured benzils react readily with *o*-phenylenediamine with formation of quinoxalines and are readily oxidised by hydrogen peroxide to two molecules of substituted benzoic acids. The observation has now been made that the colourless benzils exhibit neither of these reactions with facility. The colourless compounds often give pale yellow solutions, and this suggests the existence of an equilibrium :



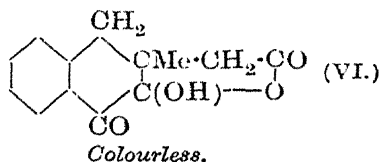
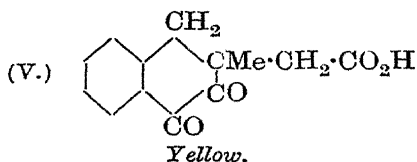
It is in fact found that the reactivity of a benzil is roughly proportional to the intensity of colour of its solution. Finally, in 4 : 4'-dibenzoyloxybenzil,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\text{Ph}$  (IV), a substance has been discovered which can be isolated in bright yellow diketonic and colourless peroxidic forms.

The latter is obtained by quickly cooling a concentrated ethereal solution of the substance. It crystallises in colourless needles which become yellow at 121° and melt indefinitely at 124°. This is the labile modification and if allowed to remain in contact with the solvent passes into solution, whilst yellow prisms of the more stable diketonic form, melting sharply at 126°, grow at its expense. The two substances are distinguished by their differing behaviour with reagents in the sense already indicated, so that this is a true case of tautomerism involving two chemical individuals which are in equilibrium in solution. Both yellow and colourless forms are unimolecular in solution and this is also true of benzils which exist

<sup>71</sup> A. Schönberg and O. Kraemer, *Ber.*, 1922, 55, [B], 1174; *A.*, i, 663; A. Schönberg and W. Bleyberg, *ibid.*, 3753.

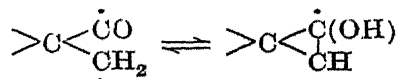
<sup>72</sup> *T.*, 1907, 91, 541. The substance first saw the light, which it refused to absorb, in the chemical laboratories of the University of Leipzig. The comment of Wislicenus, "*Das ist kein benzil*," does not appear to have been far from the mark.

exclusively in yellow or colourless modifications respectively. Thus 2 : 2 -diethoxybenzil is unimolecular in its colourless solutions. The phenomenon is accordingly not at all analogous to the polymerisation of coloured nitroso-compounds to colourless dimerides. One consequence of this work and that of Willstätter is to dispose of the idea that the colour of the  $\alpha$ -diketones and of the quinones is due to oscillations between diketonic and peroxidic forms. In solutions in which equilibrium is established the colour is of feeble intensity on account of the lower concentration of the coloured modification. Another new type of tautomerism (ring-chain), which can be followed by a colour change due to the production of an  $\alpha$ -diketonic group, is exhibited by the remarkable compound having the constitution VI.



The substance clearly fulfils the requirements of true tautomerism and can be converted into derivatives from the diketonic form (V) or from the lactonic form (VI). With *o*-phenylenediamine, it yields a quinoxaline, and oxidises as a diketone when treated with hydrogen peroxide. On the other hand, acetylation produces the acetyl derivative of the keto-lactone. The colourless solution in water becomes yellow on heating and colourless again on cooling and it is important to notice that the same change occurs in neutral solvents, although more slowly.<sup>73</sup> In alkaline solution there is evidence of ring-chain tautomerism of another kind, but this is best discussed in connexion with a different example which has the added interest that the occurrence of the phenomenon was anticipated as the result of theoretical considerations.<sup>74</sup>

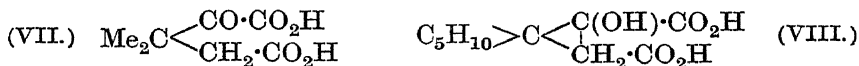
The ordinary keto-enol isomeric change may be regarded as a reversible aldol-type condensation involving a carbonyl group and the methylene group, activated by itself, often, however, assisted in the latter function by other groups such as the carbethoxyl in ethyl acetoacetate. In suitably constituted substances, the carbonyl and methylene groups might be separated by a chain of atoms, and the object of the work now under discussion was to find such a case in which the separation is by one carbon atom. In other words, to realise the equilibrium :



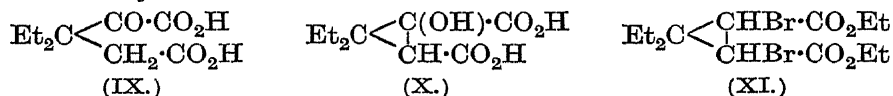
<sup>73</sup> G. A. R. Kon, A. Stevenson, and J. F. Thorpe, *T.*, 1922, 121, 650.

<sup>74</sup> S. S. Deshapande and J. F. Thorpe, *ibid.*, 1430.

The series chosen for investigation was that of the  $\alpha$ -ketoglutaric acids, and earlier work had shown that  $\alpha$ -keto- $\beta\beta$ -dimethylglutaric acid exists in the open-chain form (VII), whilst the related *cyclohexane* derivative prefers the hydroxy-ring arrangement (VIII).



This was explained in terms of a hypothesis relating to the effect of attached groups on the carbon tetrahedral angle. The two methyl groups in VII do not bring the methylene and carbonyl groups into sufficiently close proximity, whilst the effect of the *cyclohexane* ring in VIII is to cause them to approach so close to one another that the *cyclopropane* ring is readily formed and also stable. In order to realise tautomerism it was desirable to find substituting groups in the  $\beta$ -positions which would have an effect greater than that of *gem*-dimethyl and less than that of penta-methylene. Theoretically, this should be found in the *gem*-diethyl group, and  $\alpha$ -keto- $\beta\beta$ -diethylglutaric acid (IX) was accordingly prepared by the action of very concentrated, hot aqueous potassium hydroxide on ethyl  $\alpha\alpha'$ -dibromo- $\beta\beta$ -diethylglutarate (XI). The conditions can be so adjusted that either the acid (IX) or the hydroxy-ring acid (X) constitutes the main product, and the two substances can be separated by means of ether, which dissolves the former only.

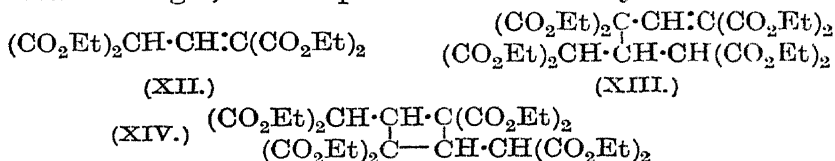


These compounds are not themselves tautomerides, but a tautomeric equilibrium of their salts is set up in a concentrated solution of potassium hydroxide (64 per cent.). The equilibrium mixture reached from either side contains approximately 38 per cent. of the keto-form. The tendency of this series of researches is to show that tautomerism of the ring-chain type may be anticipated as the result of reversible intramolecular additions analogous to all known intermolecular reversible additive reactions capable of joining two chains. Stereochemical considerations, and those connected with reactivity in general, are introduced in order to arrive at suitable test cases. Just as the keto-enol change is the simplest example of the reversible addition of  $-\text{CH}_2$  to  $-\text{C}=\text{O}$ , so the glutaconic acid, three-carbon tautomerism is the simplest known case of reversible addition of  $-\text{CH}_2-$  to  $-\text{C}=\text{C}$ . Now the best known reversible intermolecular reaction of the latter kind is the Michael condensation, and an exhaustive investigation <sup>75</sup> has

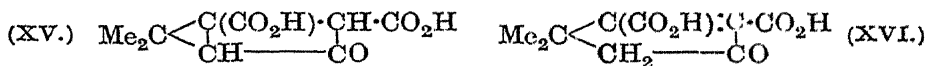
<sup>75</sup> C. K. Ingold, E. A. Perren, and J. F. Thorpe, *T.*, 1922, 121, 1765.



brought to light several examples of ring-chain tautomerism in which the equilibrium set up is strictly analogous to that resulting when sodiomalonic ester is allowed to react with an  $\alpha\beta$ -unsaturated ester.<sup>76</sup> A summary of the whole of the work on this subject cannot even be attempted, but an isolated example may be mentioned. The action of piperidine on ethyl dicarboxyglutaconate (XII)<sup>77</sup> leads to the formation of the esters XIII and XIV in successive stages, and the process is reversed by sodium ethoxide.



The individuals XIII and XIV can be separated and isolated, the former being a liquid and the latter a solid, melting at 103°. The two substances have, however, been shown to be in tautomeric equilibrium in a solvent or at slightly higher than normal temperatures so as to avoid the disturbance produced by crystallisation. The mixture contains about 80 per cent. of the cyclic ester (XIV) and the attainment of equilibrium is much facilitated by the addition of piperidine, although not absolutely dependent on this. Although the isomeric changes involved are far more sluggish than those with which we are familiar in the case of ethyl acetoacetate, the claim is justified that the term tautomerism is equally applicable to both examples. When ring-chain tautomerism involves the production of a bridge in a substance already cyclic, it is called intramolecular tautomerism and the distinction is not only convenient but also desirable from the point of view that what may be called the chemical potential of the groups involved need not be so great as in ring-chain tautomerism owing to the close space relationship of some of the constituent atoms of a ring. It has already been shown that the acid XV behaves in some of its reactions as if it had the formula XVI.<sup>78</sup>



An even more complete investigation of the decarboxylated acid (XVII) has now been carried out with results which demonstrate the existence of the indicated equilibrium.<sup>79</sup> The question of the formula to be assigned to the solid acid has not yet been answered.

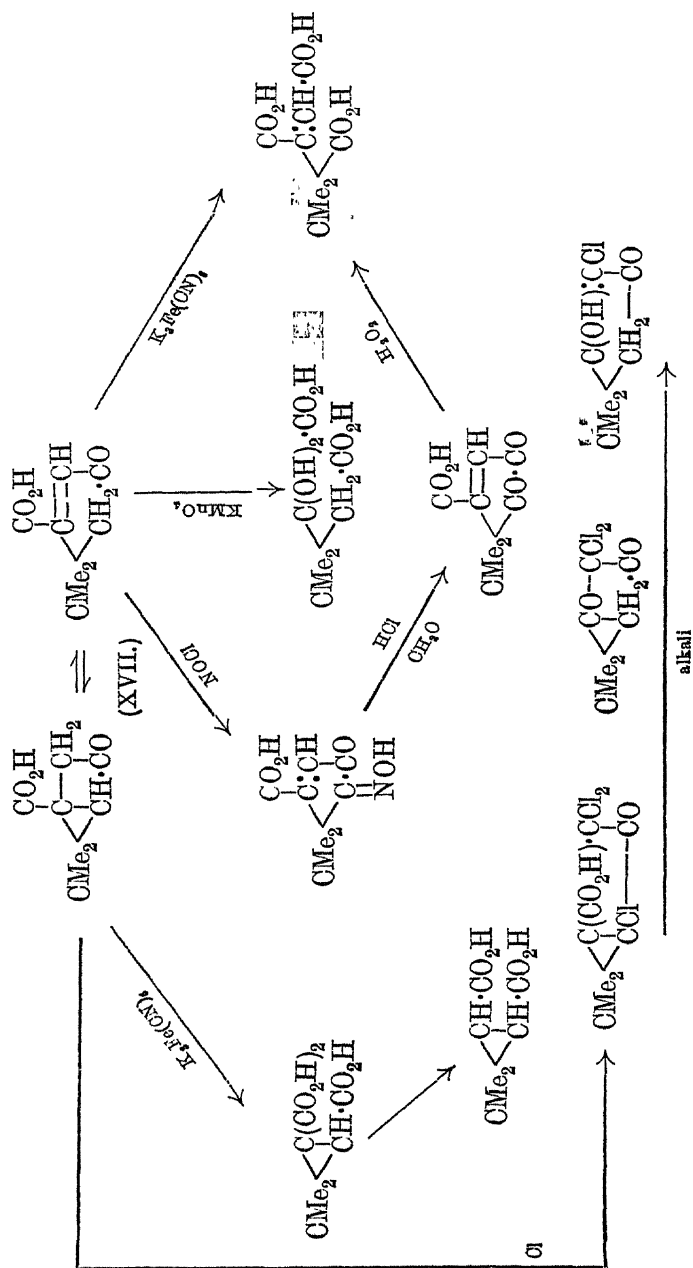
<sup>76</sup> C. K. Ingold and E. A. Perren, *T.*, 1922, 121, 1582; C. K. Ingold and W. J. Powell, *ibid.*, 1796.

<sup>77</sup> Guthzeit, *Ber.*, 1901, 34, 675; Guthzeit, Weiss, and Schafer, *J. pr. Chem.*, 1909, [ii], 80, 412.

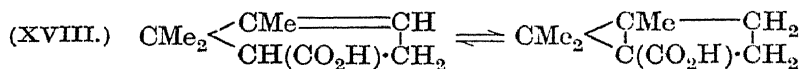
<sup>78</sup> E. H. Farmer and C. K. Ingold, *T.*, 1920, 117, 1362.

<sup>79</sup> E. H. Farmer, C. K. Ingold, and J. F. Thorpe, *ibid.*, 1922, 121, 128.

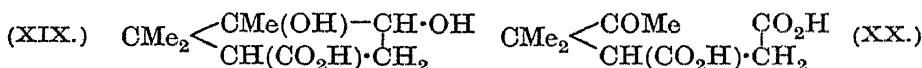
The following relations illustrate a part of the proof of the separate existence of the isomerides which is offered.



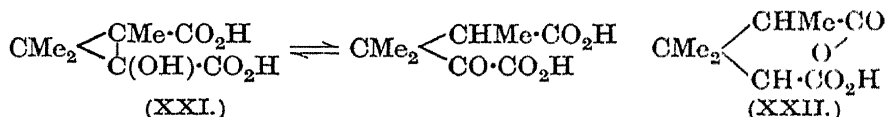
This again is a perfectly clear case in which the reaction involved is analogous to the Michael condensation, being an addition of  $-\text{CH}_2-$ ,  $\alpha$ - to carbonyl, to an  $\alpha\beta$ -unsaturated ketone. Analogies are not, however, so readily found for another case of intra-annular tautomerism which is now suspected to occur in the well-known substance,  $\alpha$ -campholytic acid (XVIII).<sup>80</sup>



The discussion of the evidence, which is based on a study of the oxidation of the acid under various conditions, involves a closely reasoned and somewhat complex argument which does not lend itself to summarisation. The following are some of the points. Alkaline permanganate oxidises  $\alpha$ -campholytic acid to the glycol XIX and the keto-dibasic acid XX and this is consistent with the double-bonded formula only.



On the other hand, acidified chlorate and osmium tetroxide in the cold produces several products, among which are found the tautomeric substance often called Balbiano's acid (XXI) and a lactonic acid of the formula XXII.



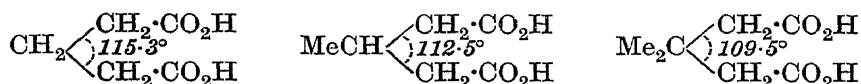
The latter substance was compared with a specimen synthetically prepared. These and other results are regarded as proving that  $\alpha$ -campholytic acid also exists in the bridged-ring form and that the substance exhibits intra-annular tautomerism. It is certainly difficult to imagine a different interpretation of the results, but the proof is not quite so conclusive as in some of the other new cases of tautomerism, because it depends wholly on the course of degradations which *might* involve some obscure transformation.

#### Ring Formation.

The value of the theory connecting the angles between carbon-to-carbon valencies and the atomic volumes of the attached groups is confirmed in a general way by the correspondence between the anticipated order of sequence in a series of substances and the facts observed in relation to such properties as the ease of formation

<sup>80</sup> J. P. C. Chandrasena, C. K. Ingold, and J. F. Thorpe, *T.*, 1922, **121**, 1542.

of cyclic compounds. In the three compounds glutaric acid,  $\beta$ -methylglutaric acid, and  $\beta\beta$ -dimethylglutaric acid, the calculated angles are as indicated and it has been shown that the ease of formation of the *cyclopropane* ring, by connecting the carbon atoms in the  $\alpha$ -positions, increases as this angle diminishes.



The method adopted was similar to that used previously and consisted in estimating as far as possible all the products formed by the treatment of the esters of the  $\alpha$ -bromo-acids with alkali under standard conditions. In the following table, taken from the original,<sup>81</sup> the new data are those for the  $\beta$ -methylglutaric acid series and it should be noted that the amount of *cyclopropane* acids quoted includes the products which can only have been derived by subsequent decomposition of these substances.

Products.	Derivatives from		
	glutaric acid per cent.	$\beta$ -methyl- glutaric acid per cent.	$\beta\beta$ -dimethyl- glutaric acid per cent.
$\alpha$ -Hydroxyglutaric acids .....	16	8	4
Glutaconic acids .....	3	9	0
<i>cyclopropane</i> acids .....	47	64	84
	<hr/> 66	<hr/> 81	<hr/> 88

These results are in excellent agreement with the theory and it should be remarked that non-steric effects are to a large extent eliminated by the method chosen, which is to compare the extent of ring formation with the extent of occurrence of a side reaction, in this case hydroxylation. It is a reasonable assumption that changes in the reactivity of the bromine would be approximately equally effective in stimulating and retarding both reactions. Such results are not related, however, to the precise angles quoted in any way except by the placing of a series in a certain order. Compounds of the type  $\text{RR}'\text{C} \begin{array}{c} \swarrow \text{C}(\text{CN}) \cdot \text{CO} \\ \searrow \text{C}(\text{CN}) \cdot \text{CO} \end{array} \text{NH}$  have been prepared in

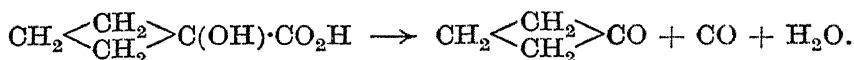
order to compare the effects of the substituents R, R' on the stability of the *cyclopropane* ring.<sup>82</sup> Previous work had shown that when R and R' are methyl, the hydrolysis of the complex gives an open-chain hydroxy-acid (lactone), whilst, under similar conditions, the three-carbon ring remains intact when CRR' is *cyclohexylene*. But this characteristic stability is destroyed by the substitution of a methyl group in positions 3 or 4 in the *cyclohexane* ring; a very

<sup>81</sup> C. K. Ingold, *T.*, 1922, **121**, 2676.

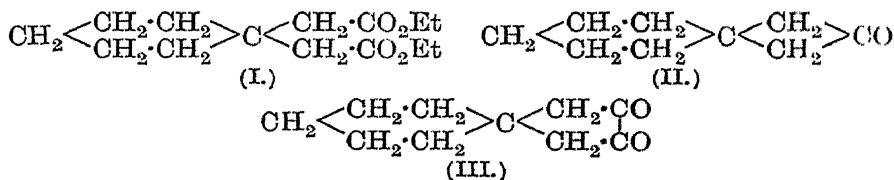
<sup>82</sup> S. F. Birch and J. F. Thorpe, *ibid.*, 1821.

remarkable result which would seem to imply a steric effect at a distance, possibly having some connexion with the varieties of buckling, of which the *cyclohexane* ring appears to be capable. In relation to this subject it may be noted that *cis*- and *trans*-*cyclohexane*-1:2-dicarboxylic acids both form inner anhydrides, of which the former is the more stable and is produced from the *trans*-anhydride on heating.<sup>83</sup>

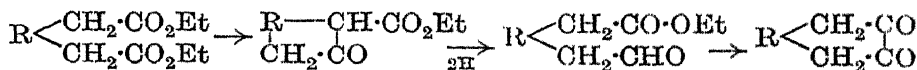
It has frequently been observed that ease of formation and stability of cyclic systems are not necessarily parallel and the *cyclobutane* series furnishes some of the best examples. Thus *cyclobutanone*, hitherto a very inaccessible compound, may be obtained in a yield of 15 per cent. by the pyrogenic decomposition of 1-hydroxy*cyclobutane*-1-carboxylic acid and is consequently a very stable substance.<sup>84</sup>



In contrast, *cyclobutanone* derivatives can only be prepared by the aid of the Dieckmann reaction in exceptionally favourable cases and then only in very poor yields. Ethyl *cyclohexane*-1:1-diacetate (I) reacts with potassium in xylene solution with formation of a mixture of products from which *cyclohexanespirocyclobutanone* (II) and *cyclohexanespirocyclopentane*-3:4-dione (III) can be isolated.<sup>85</sup>



The *cyclobutanone* derivative is a stable saturated ketone, which is unfortunately obtained in a yield amounting to little more than 1 per cent. Its formation is an indication that the Dieckmann reaction occurs, but does not prove this, as the ketone might have been derived from III by a degradation similar to that which phenanthraquinone suffers in its change to fluorenone. The suggested mechanism of formation of the diketone III is the following:



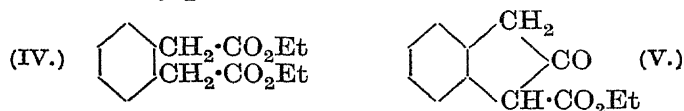
<sup>83</sup> A. Windaus and W. Hüchel, *Nachr. Ges. Wiss. Göttingen, Math. phys. Klasse*, 1920, 11, ii, 181; *A.*, i, 658.

<sup>84</sup> W. J. Demjanov and (Miss) M. Dojarenko, *Ber.*, 1922, 55, [B], 2737; *A.*, i, 1161.

<sup>85</sup> G. A. R. Kon, *T.*, 1922, 121, 520.

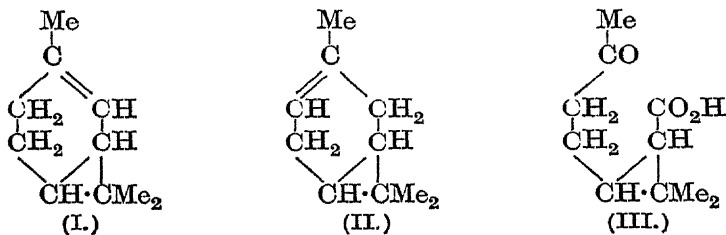
It seems simpler to regard it as a pinacol-like reduction of the carbethoxyl groups thus:  $-\text{CO}_2\text{Et} + \text{K} \rightarrow \text{C}(\text{OK})\cdot\text{OEt}$ ;  $2\text{C}(\text{OK})\cdot\text{OEt} \rightarrow -\text{CO}\cdot\text{CO}- + 2\text{KOEt}$ . The diketone may then be reduced to a keto-alcohol, and this view is supported by the fact that ethyl diethoxyacetate reacts with potassium with formation of the ketonic alcohol,  $(\text{EtO})_2\text{CH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OEt})_2$ .<sup>86</sup>

A systematic investigation of the application of the Dieckmann reaction to the preparation of benzoketopolymethylenes has been commenced by a study of one of the more favourable cases. The action of sodium at  $100^\circ$  on a toluene solution of ethyl *o*-phenylenediacetate (IV) causes the separation of the sodium derivative of ethyl 2-hydrindone-1-carboxylate (V) in a yield of 90 per cent. of that theoretically possible.<sup>87</sup>



#### *Natural Products.*

The terpene present in the essential oil from *Andropogon Jwarancusa*, Jones, appears to be  $\Delta^4$ -carene (I). This conclusion is based on the following facts.<sup>88</sup> The hydrocarbon is dicyclic, as it forms a dibromide and a monohydrochloride in ethereal solution. In acetic acid solution, it forms a dihydrochloride, identified as dipentene dihydrochloride, and in addition an oily dihydrochloride, probably that of sylvestrene, because the regenerated terpene gives the highly specific reaction with acetic anhydride and sulphuric acid. This indicates very clearly a hydrocarbon of the carene group. In contradistinction from the  $\Delta^3$ -carene (II), which has been proved to occur in the oil of *Pinus longifolia*,<sup>89</sup> the molecular refraction showed considerable exaltation, which is in agreement with the suggested formula.



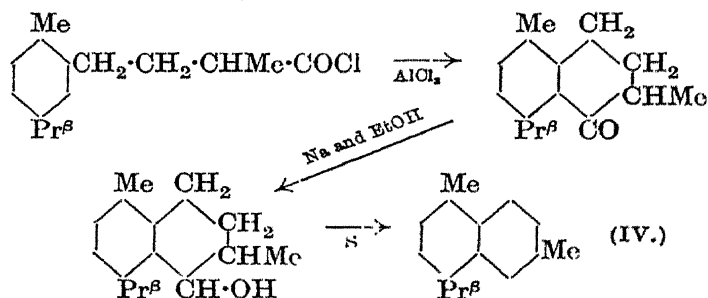
<sup>86</sup> A. Wohl and B. Mylo, *Ber.*, 1912, 45, 322.

<sup>87</sup> W. H. Perkin and A. F. Titley, *T.*, 1922, 121, 1562.

<sup>88</sup> J. L. Simonsen, *ibid.*, 2292.

<sup>89</sup> *Ibid.*, 1920, 117, 570.

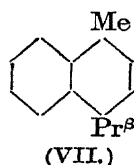
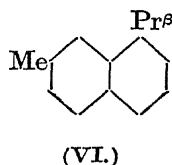
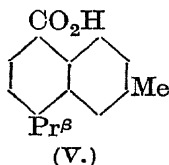
The results of permanganate oxidation are consistent with the carene structure, since the main product is an optically active acid isomeric with pinonic acid. It probably has the constitution III and is changed by hypobromite into bromoform and an isomeride of pinic acid. The ease with which the ring may be opened is an argument in favour of the *cyclopropane* formula. It is remarkable that two members of the carene group, which had not previously been found to occur in nature, should have been isolated by one investigator during such a short period of time. A substantial accretion to our knowledge of the sesquiterpenes has resulted from an investigation of the nature of the aromatic compounds which are produced from them by heating with sulphur.<sup>90</sup> Dehydrogenation in this way converts cadinene, tetrahydrocadinene, calamenol, calamene, calamenene, zingiberene, *isozingiberene*, and the sesquiterpene from Javanese citronella oil into one and the same hydrocarbon,  $C_{15}H_{18}$ , termed cadalene. This is clearly a naphthalene derivative and on the assumption that the relation of the open-chain alcohol, farnesol, to cadinene is analogous to that of a typical olefine terpene alcohol of the  $C_{10}$ -group to a *p*-cymenoid terpene, the guess was made that cadalene should be 1 : 6-dimethyl-4-*iso*-propylnaphthalene (IV). A synthesis of the latter hydrocarbon was carried out and the substance was found to be identical with cadalene. The later stages are indicated below :



Very valuable information regarding the carbon skeleton of some sesquiterpenes is thus obtained, but the reservation is made that since zingiberene is monocyclic it is evident that the naphthalene ring is to be regarded as only potentially present in the molecule. When eudesmol and selinene are heated with sulphur, a hydrocarbon,  $C_{14}H_{14}$ , called eudalene, is produced. This also is a naphthalene derivative and its production is supposed to be due to the occurrence in the parent molecule of a methyl group which cannot

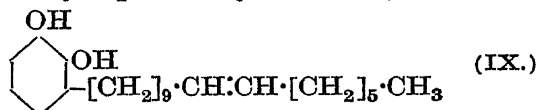
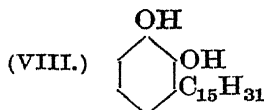
<sup>90</sup> L. Ruzicka, J. Meyer, and M. Mingazinni, *Helv. Chim. Acta*, 1922, 5, 345; *A.*, i, 560; L. Ruzicka and C. F. Seidel, *ibid.*, 369; *A.*, i, 562; L. Ruzicka and M. Mingazzini, *ibid.*, 710; *A.*, i, 1001.

survive the transition into an aromatic compound. A similar case is the production of retene from abietic acid. Cadalene (IV) on oxidation with chromic acid yields a naphthoic acid,  $C_{15}H_{16}O_2$ , which must have the constitution V because it can be converted to a methylisopropynaphthalene (VI) which is not identical with the synthesised 1-methyl-4-isopropynaphthalene (VII).

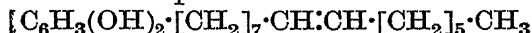


Neither VI nor VII is identical with eudalene, which is therefore not an *apocadalene* as was at first supposed. Ruzicka and his collaborators have also attacked the problem of the constitution of abietic acid, but the discussion of the results as well as of those of Windaus and his co-workers on cholesterol, the bile-acids, and allied subjects must be deferred. It is not too optimistic to hope that a little more information will enable the final elucidation of these problems to be chronicled.

The main constituent of Japanese lac is a mixture, called urushiol, containing 10 per cent. of hydrourushiol, into which all the other constituents are converted by reduction. Hydrourushiol has already been shown to be 2 : 3-dihydroxy-*n*-pentadecylbenzene (VIII).



The products of the action of ozone on urushiol diacetate and dimethyl ether are such as can be explained by the supposition that urushiol contains the compounds



and  $C_6H_3(OH)_2 \cdot [CH_2]_7 \cdot CH:CH \cdot [CH_2]_4 \cdot CH:CH_2$ .<sup>91</sup> The main constituent of Indo-Chinese lac called "laccol" has the constitution IX.<sup>92</sup> Its dimethyl ether yields a mono-ozonide which is decomposed by boiling water with formation of heptaldehyde, nonane- $\omega\omega'$ -dicarboxylic acid, and an aldehyde of the composition  $C_6H_3(OMe)_2 \cdot [CH_2]_9 \cdot CHO$ . The simultaneous formation of acet-aldehyde and formic acid as well as of more complex fatty-aromatic aldehydes indicates the occurrence of constituents of laccol other than IX, but these are probably all closely related. Hydrolaccol dimethyl ether forms a mononitro- and a dinitro-derivative and the latter fact suffices to prove that the substance cannot be a 4-sub-

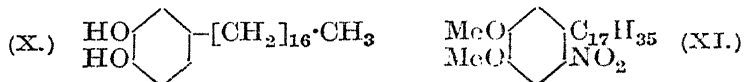
<sup>91</sup> R. Majima, *Ber.*, 1922, 55, [B], 172; *A.*, i, 262.

<sup>92</sup> *Ibid.*, 191; *A.*, i, 263.



stituted veratrole. The outcome of the attempt to dinitrate 4-alkylveratroles is invariably to produce 4:5-dinitroveratrole as the result of displacement.

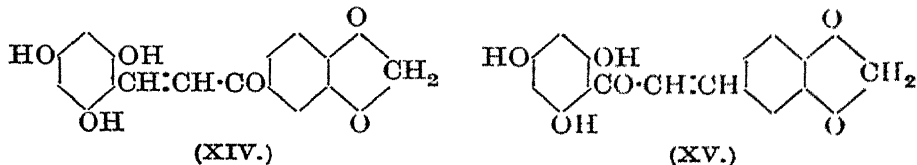
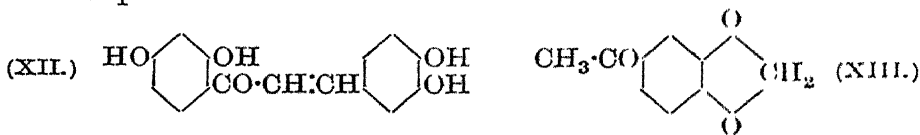
Burmese lac contains "thitsiol" reducible to hydrothitsiol, which is shown to be 4-*n*-heptadecylcatechol (X) by direct synthesis. Margarinic acid is condensed with catechol in presence of stannic chloride, and the 3:4-dihydroxyphenyl heptadecyl ketone is then reduced by means of amalgamated zinc and hydrochloric acid (Clemmensen).



Hydrothitsiol dimethyl ether forms only a mononitro-derivative (XI). Urushiol is accordingly but one member of a considerable group of related substances, derivatives of catechol substituted in both 3- and 4-positions by saturated and unsaturated normal chains identical with those which occur in the higher fatty acids. The novelty and interest of this work need not be emphasised.

Hyssop plants attacked by fungi contain a rhamno-glucoside, hyssopin,  $\text{C}_{50}\text{H}_{66}\text{O}_{30} \cdot 3\text{H}_2\text{O}$ , which yields hyssopinglycone,  $\text{C}_{16}\text{H}_{14}\text{O}_6$ , on hydrolysis.<sup>93</sup> The latter appears to be an analogue of butein (XII), which is produced by the action of alkali on butin, a constituent of *Butea frondosa*.<sup>94</sup> Hyssopinglycone, an ochre-yellow, crystalline substance, is hydrolysed by hot 33 per cent. aqueous potassium hydroxide with formation of phloroglucinol and acetopiperone (XIII).

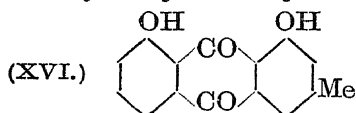
It should therefore have the formula XIV, especially since butein, when similarly treated, gives resacetophenone, but the constitution actually advanced is XV, in which the aromatic groups are transposed.



<sup>93</sup> O. A. Oesterle, *Schweiz. Apoth. Ztg.*, 1921, 59, 548; *A.*, i, 849; *ibid.*, 1922, 60, 441; *Chem. Zentr.*, 1922, iii, 1300. It has only been possible to consult the abstracts.

<sup>94</sup> A. G. Perkin and J. J. Hummel, *T.*, 1904, 85, 1459.

Chrysophanic acid has been synthesised and thus definitely proved to be 1:8-dihydroxy-3-methylanthraquinone (XVI).<sup>95</sup>



The details of the method employed follow normal lines, the starting points being  $\alpha$ -nitrophthalic anhydride and *m*-cresol. At the same time the constitutions of rhein and aloemodin are finally decided, since these two substances and chrysophanic acid are known to differ only in the side chain, which is  $-\text{CO}_2\text{H}$ ,  $-\text{CH}_2\cdot\text{OH}$ , and  $-\text{CH}_3$ , respectively.

### *Polycyclic Groups.*

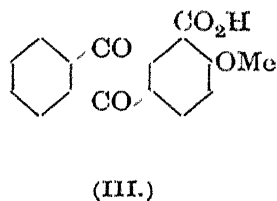
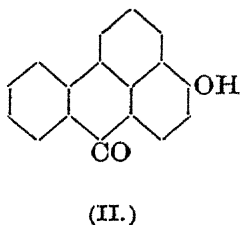
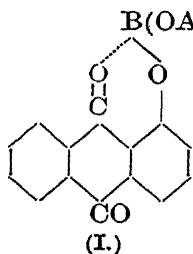
As usual, a great amount of systematic work in the naphthalene and anthracene series has been published during the past year, and the new availability of tetrahydronaphthalene has naturally been exploited to the full. In view, however, of the existence of Reports on the Progress of Technological Chemistry, the discussion of these subjects may be confined to the remark, in no way deprecatory, that the literature has been enriched by the description of vast numbers of new compounds.

In view of the importance of boric acid in the chemistry of anthracene derivatives, the isolation of definite boric compounds in the anthraquinone group is of interest.<sup>96</sup> 1-Hydroxyanthraquinone is transformed by the action of a solution of boric acid in acetic anhydride into 1-hydroxyanthraquinonyl boracetate,  $\text{C}_{14}\text{H}_7\text{O}_2\cdot\text{O}\cdot\text{B}(\text{OAc})_2$ , which loses a molecule of acetic anhydride on heating in a vacuum, yielding the metaborate,  $\text{C}_{14}\text{H}_7\text{O}_2\cdot\text{O}\cdot\text{BO}$ , but 2-hydroxyanthraquinone does not behave in a parallel manner. This is but one instance of a characteristic difference in behaviour of hydroxyl groups in the  $\alpha$ - and  $\beta$ -positions in the anthraquinone nucleus and it is clearly a question of some kind of association, in the former case, of the hydroxyl with the neighbouring carbonyl. The stability of the boracetate already mentioned can, for example, be roughly represented by formula I. This is confirmed by the facts that 1:5-dihydroxyanthraquinone reacts with two molecules of boracetic anhydride, the 1:8-isomeride with one only, and 1:4:5-trihydroxyanthraquinone suffers boracetylation of two hydroxyls and acetylation of the third. The difficulty experienced in acetylating 1-hydroxyanthraquinones is also ascribed to a mutual partial valency saturation of the hydroxyl and carbonyl groups and this theory serves to explain why chrysazin is more readily mono-

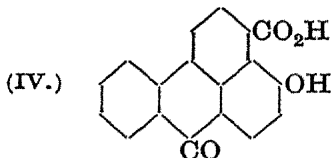
<sup>95</sup> R. Eder and C. Widmer, *Helv. Chim. Acta*, 1922, **5**, 3; *A.*, i, 260.

<sup>96</sup> O. Dimroth and T. Faust, *Ber.*, 1921, **54**, [B], 3020; *A.*, i, 155.

acetylated than anthrarufin. The carbonyl group is supposed to be unable to neutralise more than one of the hydroxyls in the  $\alpha$ -position. Relations between the quinone oxygen and auxochromes in the  $\alpha$ -position have also been postulated in order to account for the tinctorial and dyeing properties of members of the anthraquinone group and it is worthy of note that the more useful dyestuffs belong to the 1 : 4- or 1 : 5-series, in which both carbonyls can so function. In addition, the plan of increasing the number of auxochromes in anthraquinone dyestuff-types seldom produces the desirable results which may have been anticipated. In the chlorate-alkali fusion of benzanthrone, which converts this substance into 2-hydroxybenzanthrone (II) it has been found that the yield becomes almost quantitative when anthraquinone is added to the mixture.<sup>97</sup> The constitution of the substance, which may also be obtained by the action of glycerol and sulphuric acid on 2-hydroxyanthranol, has been proved by the identification of the product of oxidation of its methyl ether with 2-methoxyanthraquinone-1-carboxylic acid (III).<sup>98</sup>



Reduction of anthraquinone to anthranol is readily effected by heating with dextrose and alkali solution under pressure,<sup>99</sup> but when the reaction was applied to 2-hydroxyanthraquinone the main product was the acid IV. This readily forms a lactone and its methyl ether yields III and other substances on oxidation. It is possible to replace the dextrose used by other carbohydrates, and even by glycerol, which must clearly undergo condensation before it can supply the necessary chain of four carbon atoms.<sup>1</sup>



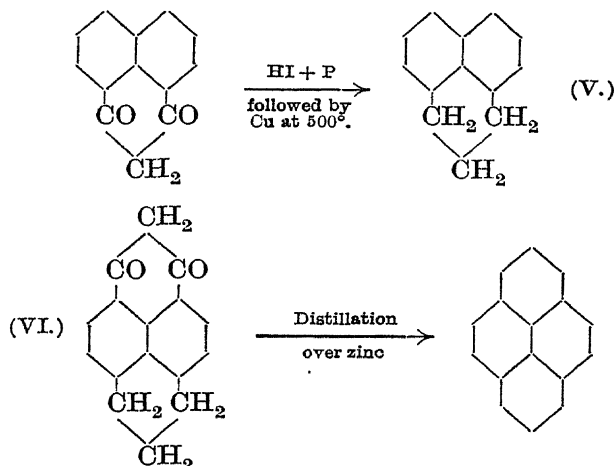
<sup>97</sup> A. G. Perkin and G. D. Spencer, *T.*, 1922, 121, 474.

<sup>98</sup> A. G. Perkin, *ibid.*, 1920, 117, 698.

<sup>99</sup> *Idem.*, Brit. Pat. 151707, 1920.

<sup>1</sup> G. G. Bradshaw and A. G. Perkin, *T.*, 1922, 121, 911.

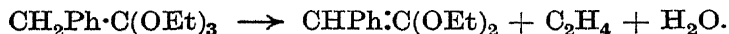
A direct synthesis of pyrene from naphthalene has been carried out and the stages are as indicated in the following scheme. The starting point is obtained by the condensation of naphthalene and malonyl bromide in presence of aluminium chloride, and the substance VI by an analogous method applied to V.<sup>2</sup>



#### Miscellaneous.

**Benzaldehyde-copper.**—Nickel, iron, and aluminium have no action on benzaldehyde, but lead and magnesium dissolve to a yellowish-brown solution, zinc to a greenish-brown, silver to a brownish-black, cobalt to a brown, and copper to a green solution. In the case of copper, the substance formed is a green additive product,  $(\text{Ph}\cdot\text{CHO})_2\text{Cu}$ , which can be crystallised from toluene. It is remarkably stable, being unattacked by dilute hydrochloric acid or alkalis, but is oxidised to benzoic acid by dilute nitric acid. The constitution of the compound is not yet clear, the obvious possibility that it is copper hydrobenzoin being difficult to reconcile with the stability to acid.<sup>3</sup>

**Enolisation of Acids.**—The acetal of phenylketen can be prepared by careful distillation of the ortho-ester of phenylacetic acid with phosphoric acid in a vacuum : <sup>4</sup>



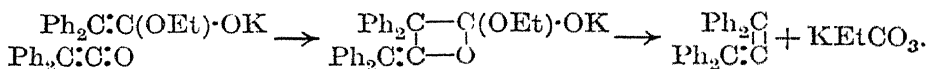
Compared with keten, it is quite stable, but is attacked by water with formation of ethyl phenylacetate and by bromine with formation of ethyl phenylbromoacetate. The metallic derivatives of

<sup>2</sup> K. Fleischer and E. Retze, *Ber.*, 1922, 55, [B], 3280; *A.*, i, 1138.

<sup>3</sup> A. L. Bernoulli and F. Schaaf, *Helv. Chim. Acta*, 1922, 5, 721; *A.*, i, 1029.

<sup>4</sup> H. Staudinger and G. Rathsam, *ibid.*, 645; *A.*, i, 1014.

carboxylic esters such as malonic ester are in all probability analogously constituted and contain the group  $\text{:C(OEt)·OM}$ . This hypothesis is supported by the behaviour of the potassio-derivatives of diphenylacetic acid and its ester, since these are highly unsaturated substances.<sup>5</sup> Potassamide reacts with ethyl diphenylacetate in liquid ammonia to form an additive product which, on heating in a vacuum at 100—120°, loses ammonia, yielding potassoxyethoxydiphenylketen,  $\text{CPh}_2\text{:C(OEt)·OK}$ . This salt is spontaneously oxidised by oxygen and on treatment with methyl iodide gives ethyl  $\alpha\alpha$ -diphenylpropionate,  $\text{CPh}_2\text{Me·CO}_2\text{Et}$ . It reacts with diphenylketen to form tetraphenylacetone and tetraphenylallene and although the production of the latter is said to be difficult to explain, it appears to fall into line with the usual schemes of addition and division :



The reaction affords further proof, if that were necessary, of the constitution assigned to the potassium derivative. When potassium diphenylacetate is treated with potassamide in liquid ammonia solution, it yields an amorphous, yellow precipitate of the composition and formula,  $\text{CPh}_2\text{:C(OK)}_2$ . This substance is at once oxidised by oxygen with production of an explosive peroxide, but careful treatment in toluene solution with air gives a monoxide probably

having the structure,  $\text{Ph}_2\text{C} \begin{array}{c} \diagup \\ \text{O} \end{array} \text{C(OK)}_2$ , because aqueous acids or

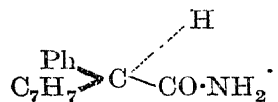
alkalis change it into benzilic acid. Alkylation of the dipotassoxy-compound with methyl iodide produces potassium  $\alpha\alpha$ -diphenylpropionate, whilst the action of methyl sulphate results in the formation of the corresponding methyl ester. These experiments provide further evidence that the metallic derivatives of the enolised forms of esters are directly alkylated on the carbon. Possibly the most satisfactory representation of sodio-compounds of the familiar type is as complex compounds, for example,  $[\text{CN·CH·CO}_2\text{Et}]\text{Na}$ , in which formula the bonds merely represent the mode of linking of atoms and have no implications in regard to the distribution of affinity. The problem of relative ease of enolisation of acids and their derivatives can also be attacked by stereochemical methods, and the racemisation of optically acid amides has been studied from this point of view.<sup>6</sup> Of the substances examined, *d*-tartamide, *d*- $\alpha$ -hydroxy- $\beta$ -phenylpropionamide,  $\text{CH}_2\text{Ph·CH(OH)·CO·NH}_2$ , *l*- $\beta$ -hydroxy- $\beta$ -phenylpropionamide,  $\text{HO·CHPh·CH}_2\text{·CO·NH}_2$ , *d*-mono-

<sup>5</sup> H. Staudinger and P. Meyer, *Helv. Chim. Acta*, 1922, 5, 656; *A.*, i, 1015.

<sup>6</sup> A. McKenzie and (Miss) I. A. Smith, *P.*, 1922, 121, 1348.

ethoxysuccinamide, and *l*-atrolactinamide,  $\text{HO}\cdot\text{CPhMe}\cdot\text{CO}\cdot\text{NH}_2$ , were not racemised in cold alcoholic solution in presence of small quantities of potassium hydroxide. On the other hand, *d*-dimethoxysuccinamide, *l*-monomethoxysuccinamide, and *l*-mandeloethylamide were slowly racemised in similar circumstances, and *l*-mandelamide, *l*-phenylmethoxyacetamide, and *l*-phenyl-*p*-tolylacetamide exhibited the phenomenon with increasing facility in the order named.

The latter observation is explained by the increased mobility of the hydrogen atom in the  $\alpha$ -position which is the result of the high valency demands of the alkyloxy and aryl groups as illustrated in the expression :



There has been much activity during the year in connexion with aryl derivatives of boron, phosphorus, arsenic, chromium, bismuth, lead, thallium, and other elements, but it has not been found possible to include a section dealing with the results, which are nevertheless of very considerable interest.

R. ROBINSON.

### PART III.—HETEROCYCLIC DIVISION.

THERE are no outstanding features to which particular attention may be directed in this Report. Rather the year has been one of quiet progress and consolidation of previous work, involving in several directions a revision of earlier conclusions.

#### *Ring Formation and Stability.*

Some years ago, it was suggested <sup>1</sup> that the points of attachment to a carbon atom of two groups, known to exert steric hindrance, are normally, in virtue of their large molecular volume, further apart than would be indicated by the regular tetrahedral distribution. The view has since been developed <sup>2</sup> that, in general, each atom attached to a carbon atom occupies a spherical domain,

<sup>1</sup> J. Kenner, *T.*, 1914, **105**, 2688.

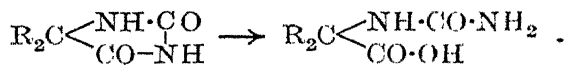
<sup>2</sup> C. K. Ingold, *ibid.*, 1921, **119**, 305.

the cubic content of which is proportional to its atomic volume. By calculation on this basis, the following values were deduced for the angle,  $2\delta$ , subtended by two carbon atoms attached to a central carbon atom, carrying two other groups,  $RR'$  :

$RR'$ .	H,H.	H,Me.	Me,Me.	Et,Et.	$(CH_2)_2$ .	$(CH_2)_3$ .
$2\delta$	$115.3^\circ$	$112.5^\circ$	$109.5^\circ$	$107^\circ$	$116.9^\circ$	$113.0^\circ$
$k'$	11.2	2.28	0.551	0.146	13.8	2.63

The last two values are for a pair of carbon atoms attached to a *cyclopropane* and to a *cyclobutane* ring, respectively, and are derived on the assumption that the position of these is such as to trisect the solid angle round the central carbon atom and external to the ring.<sup>3</sup> This would seem to be a logical extension of Werner's view as to the cause of the regular tetrahedral distribution of four similar groups attached to a carbon atom, and the experimental evidence in favour of the corollary appears to be a valuable confirmation of the main proposition.

In the above table,  $k'$  is proportional to the velocity constants of hydrolysis of the hydantoins by baryta :



The agreement between the order of the constants and that of the values of  $2\delta$  is regarded as confirming the accuracy of the method of calculating  $2\delta$ .<sup>4</sup> It will be noted, however, that the values quoted for  $2\delta$  are not properly applicable to this case, in which one carbon atom is replaced by a nitrogen atom, more especially as the atomic volume of the latter is very small.<sup>5</sup> The order of the corrected values for  $2\delta$  will, however, very possibly be the same and thus correspond with those of  $k'$ , although it is less certain that this will also hold for the *cyclo*-propylene and -butylene residues. It may also be suggested that other atoms than those immediately attached to the central carbon atom must be included in such considerations, and it is perhaps in recognition of this that the values quoted for the methyl and ethyl groups differ.

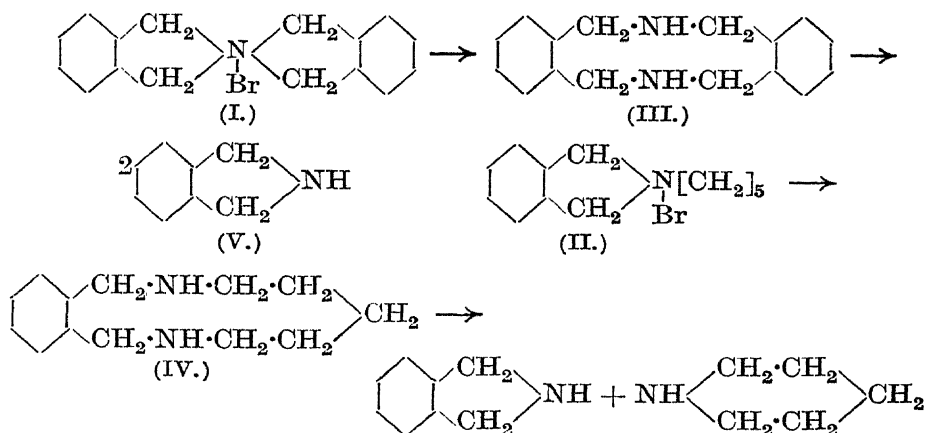
It has long been known that when the quaternary ammonium bromides (I) and (II) are heated with ammonia, they are converted into the compounds (III) and (IV) : <sup>6</sup>

<sup>3</sup> R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *T.*, 1915, **107**, 1080.

<sup>4</sup> C. K. Ingold, S. Sako, and J. F. Thorpe, *ibid.*, 1922, **121**, 1177.

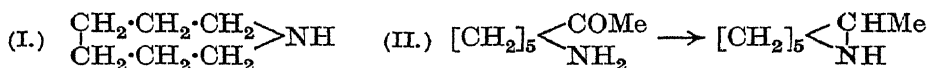
<sup>5</sup> I. Traube, *Annalen*, 1895, **290**, 119; *A.*, 1896, ii, 354.

<sup>6</sup> M. Scholtz, *Ber.*, 1891, **24**, 2402; 1898, **31**, 1700; *A.*, 1891, i, 1353; 1898, i, 567.



It may be that this change is simply due to the tendency of quaternary ammonium compounds to pass under such conditions into derivatives of trivalent nitrogen. In any case, the instability of the resulting bisimines is indicated by the fact that at  $250^\circ$  they break down into dihydroisoindole (V) accompanied in the second case by piperidine. Dihydroisoindole is in fact most conveniently prepared by heating (I) with ammonia solution at  $250^\circ$ .<sup>7</sup>

Hexamethyleneimine (I) is obtained in 50 per cent. yield by heating hexamethylenediamine hydrochloride,<sup>8</sup> although octa-<sup>9</sup> and deca-methylenediamines<sup>10</sup> furnish butyl- and hexyl-pyrrolidines, respectively. The result recalls the direct formation of 2-methylhexamethyleneimine by the reduction of methyl  $\epsilon$ -amino-amyl ketone (II):<sup>11</sup>



It will perhaps be well to consider these results, and, for example, the good yield of suberone obtainable from calcium suberate,<sup>12</sup> in the light of recent suggestions<sup>13</sup> that polymethylene rings containing more than five carbon atoms are free from tension and have not a plane configuration.

The results of earlier work<sup>14</sup> on the relative stability of cyclic

<sup>7</sup> J. v. Braun and (Miss) A. Nelken, *Ber.*, 1922, **55**, [B], 2059; *A.*, i, 863.

<sup>8</sup> F. Schmidt, *ibid.*, 1584; *A.*, i, 761.

<sup>9</sup> J. v. Braun and C. Müller, *ibid.*, 1906, **39**, 4110; *A.*, 1907, i, 28.

<sup>10</sup> F. Krafft, *ibid.*, 2193; *A.*, 1906, i, 553.

<sup>11</sup> S. Gabriel, *ibid.*, 1909, **42**, 1259; *A.*, 1909, i, 492.

<sup>12</sup> J. N. E. Day, G. A. R. Kon, and A. Stevenson, *T.*, 1920, **119**, 639.

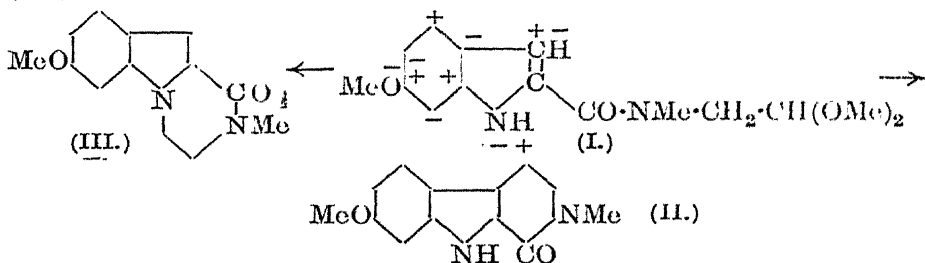
<sup>13</sup> W. Hückel, *Ber.*, 1920, **53**, 1277; *A.*, 1920, i, 603; H. G. Derx, *Rec. trav. chim.*, 1922, **41**, 312; *A.*, i, 651.

<sup>14</sup> Compare *Ann. Reports*, 1920, p. 103.



structures containing nitrogen have been supplemented and summarised.<sup>15</sup> Neither a 2-, 3-, 4-methyl-, nor a 5:6-methylene-dioxy-group affects the behaviour of *N*-methyltetrahydroquinoline methochloride towards sodium amalgam, although that of dihydroindole is considerably modified by either a 2- or a 3-methyl group.<sup>16</sup> As might be anticipated, a 2- or 3-phenyl group has a marked effect on the tetrahydroquinoline structure.<sup>17</sup> The difference between the results obtained by different methods of degrading such structures is illustrated by the case of methylisochondodendrine. By exhaustive methylation two methines are obtained, whereas the sodium amalgam method yields one product only.<sup>18</sup>

Attention was directed in last year's Report<sup>19</sup> to a compound, in which tendencies towards two distinct modes of intramolecular condensation seemed to be evenly balanced. Another instance of this kind is now provided by the conversion of 6-methoxyindole-2-carboxydimethylacetalylmethylamide (I) under the influence of alcoholic hydrochloric acid into a mixture of methoxyketomethyl-dihydrocarboline (II) and methoxyketomethyldihydroindole-diazine (III):



<sup>1</sup> It is not easy to explain the fact that the presence of the methyl group attached to the nitrogen atom in the side chain should determine carboline formation, as contrasted with the conversion of indole-2-carboxyacetalylamide itself into ketodihydroindole-diazine. If no nuclear methoxyl group be present, the course of the reaction will be entirely towards carboline formation, but it is seen from the diagram that the effect of the methoxyl group is to diminish the "positive" character of the methenyl hydrogen atom of the indole nucleus, concerned in the reaction, and to enhance that of the imino-hydrogen atom necessary for indole-diazine

<sup>15</sup> J. v. Braun and J. Seeman, *Ber.*, 1922, **55**, [B], 3818; *A.*, 1923, i, 146.

<sup>16</sup> J. v. Braun, K. Heide, and L. Neumann, *ibid.*, 1916, **49**, 2613; *A.*, 1916, i, 742.

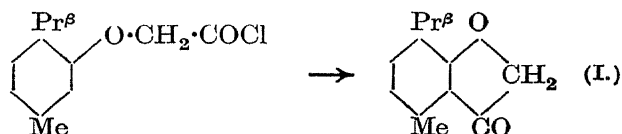
<sup>17</sup> J. v. Braun, J. Seeman, and A. Schultheiss, *ibid.*, 1922, **55**, [B], 3803; *A.*, 1923, i, 138.

<sup>18</sup> F. Faltis and F. Neumann, *Monatsh.*, 1921, **42**, 311; *A.*, i, 569.

<sup>19</sup> p. 112.

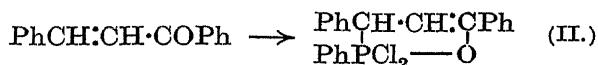
formation.<sup>20</sup> If this explanation be correct, it may be expected that a 5- or 7-methoxyl group will favour carboline formation. Such an influence of the position of methyl groups on the formation and stability of coumaranones has been noticed in previous Reports.<sup>21</sup> In this connexion, too, the results of an amplification<sup>22</sup> of earlier work on the velocities of hydrolysis of 2-substituted benzoxazoles are of interest.

A different effect of substituents, which is superimposed on that associated with their orientation, and results in a modification of the general condition of the molecule, is illustrated by the fact that neither of the three nitrophenoxyacetyl chlorides is convertible into a coumaranone,<sup>23</sup> although the reaction is otherwise a fairly general one.<sup>24</sup>



The synthesis of methylisopropylcoumaranone (I) by its aid<sup>25</sup> is another illustration of the relative independence of intramolecular condensation on steric influences.<sup>26</sup> This point stands out more clearly when it is noted that the rupture of the ring usually brought about by intermolecular hydrolysis of coumaranones, and of their isonitroso-derivatives, does not occur in this case, possibly owing to steric protection.

It is suggested<sup>27</sup> that the formation of cyclic additive products, for example (II), by interaction of aldehydes, ketones, or  $\alpha\beta$ -unsaturated ketones and phosphorus trichloride, or compounds derived from it by replacement of one or two chlorine atoms by phenyl-, phenoxy-, or ethoxy-groups,



resembles the conversion of ammonia into ammonium compounds in that in each case the tervalent atom develops two latent valencies

<sup>20</sup> W. O. Kermack, W. H. Perkin, and R. Robinson, *T.*, 1922, **121**, 1872.

<sup>21</sup> *Ann. Reports*, 1920, **16**, 101; 1921, **18**, 108.

<sup>22</sup> S. Skraup and (Miss) S. Moser, *Ber.*, 1922, **55**, [B], 1080; *A.*, i, 574; compare *Ann. Report*, 1920, **16**, 99.

<sup>23</sup> T. H. Minton and H. Stephen, *T.*, 1922, **121**, 1591.

<sup>24</sup> *Ibid.*, 1598.

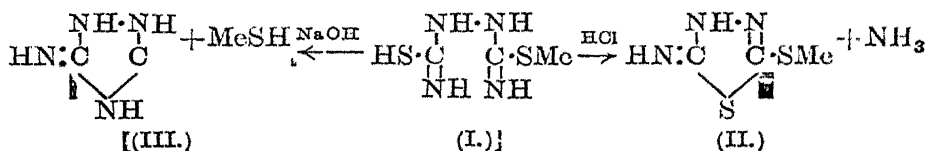
<sup>25</sup> E. Mameli, *Gazzetta*, 1922, **52**, [i], 322; *A.*, i, 669.

<sup>26</sup> Compare *Ann. Reports*, 1921, **18**, 108.

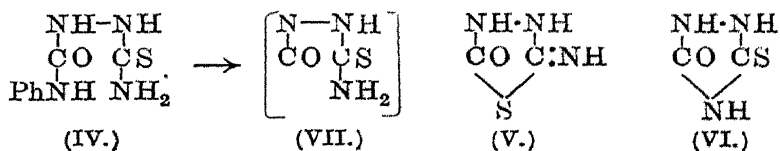
<sup>27</sup> J. B. Conant, *J. Amer. Chem. Soc.*, 1921, **43**, 1705; *A.*, i, 41; J. B. Conant, A. D. MacDonald, and A. Mc. B. Kinney, *ibid.*, 1928; *A.*, i, 186; compare *Ann. Reports*, 1920, **17**, 98.

of opposite signs.<sup>28</sup> The course of this process in its initial stages in, for example, the addition of phosphorus trichloride to a carbonyl group is conceived to be as follows. The positive nucleus of the carbon atom is assumed to be exposed, through the drawing away of its two electrons, shared with the oxygen octet, and to attract unshared electrons of the phosphorus atom. In the resulting system, the oxygen and phosphorus atoms are respectively negatively and positively charged, and therefore an inner polar bond is set up between them.

The reactions of the hydrazodicarbon-mono- and -di-thiocarbon-amides provide illustrations of the principle that every chemical system tends towards that condition in which the maximum of chemical neutralisation is attained.<sup>29</sup> For example, when hydrazomonomethyldicarbonylthiamide (I) is boiled in acid solution, the basic iminothiodiazole methyl ether (II) and ammonia are formed, whilst in caustic alkaline solution, the acidic iminothiourazole (III) and methyl mercaptan produced :



The constitution of the compounds of type (II) is confirmed by their synthesis by condensation of thiosemicarbazides with carbon disulphide in presence of alcoholic potassium hydroxide. An interesting case is that of the hydrazide (IV), from which in acid solution iminothiodiazolone (V), and in alkaline solution the sodium salt of thiourazole (VI) are formed as chief product :



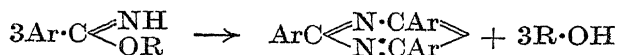
The same intermediate product (VII) may be assumed in each case.<sup>30</sup>

<sup>28</sup> Compare also (Mrs.) G. M. Robinson and R. Robinson, *T.*, 1917, 111, 958; *Ann. Reports*, 1917, 16, 134.

<sup>29</sup> A. Michael, *J. pr. Chem.*, 1899, [ii], 60, 292; *A.*, 1900, i, 321.

<sup>30</sup> F. Arndt and E. Milde, *Ber.*, 1921, 54, [B], 2089; F. Arndt, E. Milde, and F. Tschenschner, *ibid.*, 1922, 55, [B], 341; *A.*, 1921, i, 842; 1922, i, 375; compare E. Fromm, *ibid.*, 1921, 54, [B], 2840; *Annalen*, 1922, 426, 313; *A.*, i, 62, 377; P. C. Guha, *J. Amer. Chem. Soc.*, 1922, 44, 1502, 1510; *A.*, i, 875, 876.

The formation of cyaphenines by distillation of aryliminoalkyl ethers

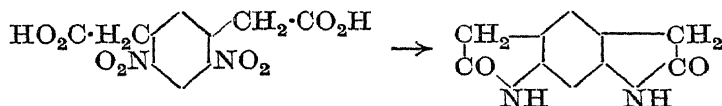


is attributed to special reactivity of nascent nitriles, since these suffer polymerisation only at high temperatures or under the influence of catalysts.<sup>31</sup> The change, however, occurs, although with extreme slowness, at the ordinary temperature and therefore might possibly consist in polymerisation, followed by elimination of alcohol.

Reference has previously been made to the difficulty frequently attaching to the production of systems containing rings in straight alignment on either side of a benzene ring.<sup>32</sup> This is noticeable in the poor yield of 2 : 3-naphthindigotin from 3-carboxy-2-naphthylglycine : <sup>33</sup>



In passing, it may be noted that 8-carboxy-1-naphthylglycine could not be converted into a *peri*-naphthindigotin.<sup>34</sup> Again, when 6-aminotetrahydroquinoline was submitted to the quinaldine synthesis, a phenanthroline resulted.<sup>35</sup> On the other hand, 2 : 6-dihydroxy-*m*- $\alpha\alpha$ -benzbispyrrole is readily produced by reduction of 4 : 6-dinitrophenylene-1 : 3-diacetic acid with ferrous sulphate and ammonia : <sup>36</sup>



Two instances of the indirect formation of structures of the general form just referred to may also be noticed here, although the primary reaction does not involve a benzene nucleus. In each case the starting material is 2 : 3-dichloro- $\alpha$ -naphthaquinone. This, by successive treatment with aniline and with sodium sulphide, is converted into 2-anilino-3-mercapto-1 : 4-naphthaquinone (I), from

<sup>31</sup> T. B. Johnson and L. W. Bass, *J. Amer. Chem. Soc.*, 1922, **44**, 1341; *A.*, i, 736.

<sup>32</sup> *Ann. Reports*, 1921, **18**, 109.

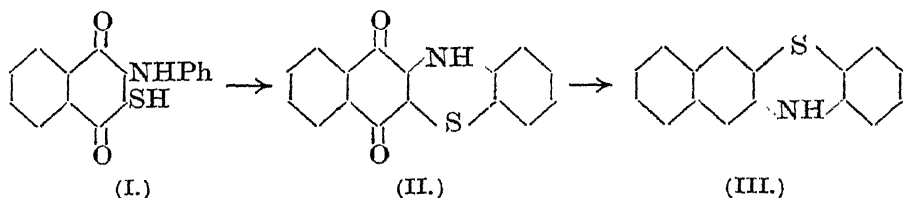
<sup>33</sup> H. E. Fierz and R. Tobler, *Helv. Chim. Acta*, 1922, **5**, 557; *A.*, i, 869.

<sup>34</sup> H. E. Fierz and R. Sallmann, *ibid.*, 560; *A.*, i, 870.

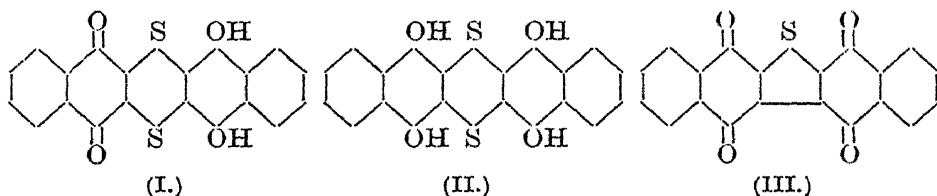
<sup>35</sup> J. Lindner, *Monatsh.*, 1921, **42**, 421; *A.*, i, 687.

<sup>36</sup> W. Davies and E. H. C. Hickox, *T.*, 1922, **121**, 2640.

which  $\beta\beta$ -naphthaphenthiazine-6:11-quinone (II) is obtained by atmospheric oxidation in alcoholic solution.



The parent naphthaphenthiazine (III) is prepared from this by energetic reduction with stannous chloride.<sup>37</sup> Again, the original quinone, when treated with sodium sulphide in absence of air, yields the green monosodium salt of the internal quinhydrone (I), from which 5:7:12:14-tetrahydroxydibenzothianthrene (II) is obtained by acid or alkaline reduction:



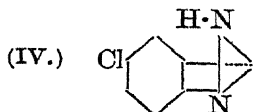
A noteworthy reaction is the elimination of sulphur with formation of dinaphthathiophendiquinone (III), when the diquinone derived from (I) is heated above its melting point in boiling nitrobenzene solution or with concentrated sulphuric acid.<sup>38</sup>

### Isomerism.

Further noteworthy cases of isomerism in the indazole series have been recorded. Freshly prepared 5-chloroindazole melts at 119–120°, but changes, slowly at the ordinary temperature, and fairly rapidly at 100°, into a modification, m. p. 143–144°. Similarly, the 5-bromo-derivative exists in a labile form, m. p. 124–125°, and a stable form, m. p. 132–133°. Since each form may be recovered unchanged after recrystallisation, they would seem not to be polymorphous. The failure to convert the high-melting into the low-melting isomerides suggests that their relationship is not one of structural isomerism, whilst the higher melting point of the stable isomerides is in agreement with the hypothesis of stereoisomerism, represented by (IV) and (V),

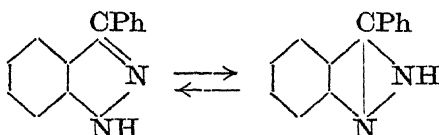
<sup>37</sup> K. Fries and F. Kerkow, *Annalen*, 1922, 427, 281; *A.*, i, 577.

<sup>38</sup> K. Brass and L. Kohler, *Ber.*, 1922, 55, [B], 2543; *A.*, i, 1050.



and already applied to the 2-acylindazoles.<sup>39</sup> In agreement with this analogy, 3-halogen indazoles do not exhibit isomerism.

A fuller investigation<sup>40</sup> of the two forms of 3-phenylindazole, m. p. 107—108° and 115—116°<sup>41</sup> has shown these to be interconvertible, and, further, it would seem that the low-melting isomeride is the more stable, since it may be obtained from the other form by distillation. The relationship is therefore considered to be one of structural isomerism :



The same explanation is adopted in the case of two forms of 3 : 5-diphenylisooxazole-4-carboxylic acid (I) and (II), and of the corresponding 5-phenyl-3-methyl-derivative.



In each case, the acid of lower melting point is converted by boiling caustic alkali into its isomeride, although the reverse change has not been accomplished. It is hoped that further information may be gained from attempts to resolve the acids into optically active components, since the compound represented by (II) should be capable of resolution.<sup>42</sup> It will be noted that the structural formulæ assigned to these pairs of compounds correspond closely with those of the tautomeric forms of dimethyldicyclopentanone-carboxylic acid.<sup>43</sup> It is interesting to note how in three distinct fields of investigation, the suggestion is almost simultaneously forthcoming that the types of bridged and unsaturated ring systems here considered are closely related. At the same time, it must be observed that although the indazoles are benzopyrazoles, the tendency on the part of pyrazoles to assume the bridged structure, if existent, is very limited.<sup>44</sup>

<sup>39</sup> K. v. Auwers and H. Lange, *Ber.*, 1922, **55**, [B], 1139; *A.*, i, 684.

<sup>40</sup> K. v. Auwers and A. Sondheimer, *ibid.*, 1896, **29**, 1255; *A.*, 1896, i, 503.

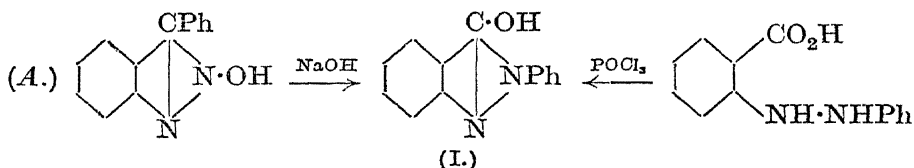
<sup>41</sup> K. v. Auwers and K. Hüttner, *ibid.*, 1922, **55**, [B], 1112; *A.*, i, 682.

<sup>42</sup> M. Betti and others, *Gazzetta*, 1915, **45**, i, 362; ii, 151, 377; 1921, **51**, ii, 229; *A.*, 1915, i, 997; 1916, i, 222; 1922, i, 52.

<sup>43</sup> E. H. Farmer, C. K. Ingold, and J. F. Thorpe, *T.*, 1922, **121**, 128.

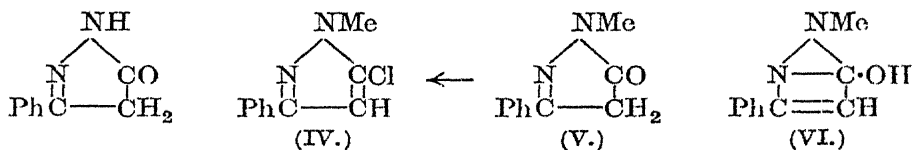
<sup>44</sup> K. v. Auwers and H. Broche, *Ber.*, 1922, **55**, [B], 3880; *A.*, 1923, i, 151.

The rearrangement of 2-hydroxy-3-phenylindazole (A), when boiled with caustic alkali, has now been shown to consist in the interchange of the hydroxyl and the phenyl groups,<sup>45</sup> since the product furnishes azobenzene-*o*-carboxylic acid on oxidation and is identical with 3-hydroxy-2-phenylindazole (I), prepared from hydrazobenzene-*o*-carboxylic acid : <sup>46</sup>



It is considered that the isomerisation depends rather on a direct interchange of the groups concerned than on the formation of any transient additive product.

Isomeric forms of five-membered cyclic compounds have also been observed in the pyrazolone series. Two isomerides result from the methylation of 3-phenyl-5-pyrazolone (II). Of these, one, m. p. 96°, is probably a methoxy-derivative, but the other, m. p. 165°, is converted by phosphorus pentachloride into 5-chloro-3-phenyl-1-methylpyrazole<sup>47</sup> (IV), identical with the product previously obtained from 3-phenyl-1-methyl-5-pyrazolone, m. p. 207°<sup>48</sup> (V) :



A similar statement in regard to the 1-phenyl-5-methyl derivative is already on record.<sup>49</sup> The suggestion is made that these pairs of compounds may be stereoisomerides represented by (VI) and of the type already mentioned in the case of the indazoles. It will, however, be noticed that no interconversion has been accomplished in the present instance and that in the case of indazoles the experimental evidence is to the effect that substitution in the position corresponding with that occupied by the hydroxyl group in (VI) inhibits stereoisomerism.

<sup>45</sup> K. v. Auwers and A. Sondheimer, *loc. cit.*

<sup>46</sup> P. Freundler, *Compt. rend.*, 1906, **143**, 909; *Bull. Soc. chim.*, 1911, [iv], 9, 738; *A.*, 1907, i, 158; 1911, i, 753.

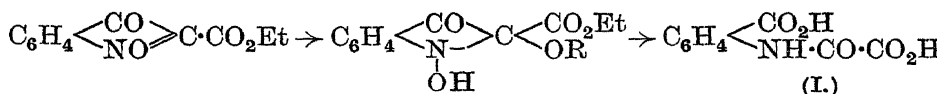
<sup>47</sup> C. A. Rojahn, *Ber.*, 1922, **55**, [E], 2959, 3990; *A.*, i, 1183.

<sup>48</sup> R. v. Rothenburg, *J. pr. Chem.*, 1895, [ii], **52**, 23; *A.*, 1895, i, 680; A. Michaelis, *Annalen*, 1907, **352**, 152; *A.*, 1907, i, 246.

<sup>49</sup> F. Stolz, *J. pr. Chem.*, 1897, [ii], **55**, 164; *A.*, 1897, i, 374.

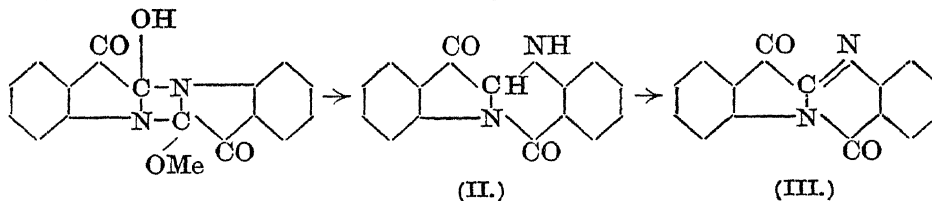
It would appear, in fact, that, apart from the careful attempts at discrimination noted in the cases of the indazoles, the suggestions made in some of the other cases just mentioned are *ad hoc* in character, and to be received with corresponding reserve.

Further, instances have not been lacking during the year which show the need for caution, before cases of alleged isomerism are finally accepted. Thus, the "isoisatogens," obtained from isatogens by the action of alcoholic hydrogen chloride,<sup>50</sup> are now stated to be in reality additive compounds of isatogens with alcohol, and to be formed, although more slowly, by treatment with alcohol alone. In the case of ethyl isatogenate, the reaction is expressed as follows :



The additive compounds are hydrolysed by cold caustic alkali to *N*-oxalylanthranilic acid (I).<sup>51</sup>

Again, the suggestion that the isatoids represent isomeric forms of isatin<sup>52</sup> has turned out to be wrong.<sup>53</sup> These compounds, more correctly termed isatoid monoalkyl ethers, were originally prepared<sup>54</sup> by interaction of alkyl iodides and the silver salt of isatin, and also from the alkylisatins, which are the first product of the reaction, by spontaneous evaporation of their benzene solutions while exposed to light. By hydrolysis, they are converted into anhydro-indoxyl- $\alpha$ -anthranilide (II), the constitution of which is indicated by its oxidation to the known anhydro- $\alpha$ -isatinanthranilide (III) :



The last compound is also obtained directly from the original ethers when their alkaline solutions are exposed to light. The existence of isomerides of isatin<sup>55</sup> is still in dispute, and it is maintained that certain of these are in reality isatoid derivatives.

<sup>50</sup> *Ann. Reports*, 1919, 15, 109; 1921, 17, 116.

<sup>51</sup> G. Heller and W. Bolsaneck, *Ber.*, 1922, 55, [B], 474; *A.*, i, 369.

<sup>52</sup> A. Hantzsch, *ibid.*, 1921, 54, [B], 1221; *A.*, 1921, i, 597.

<sup>53</sup> G. Heller and W. Benade, *ibid.*, 1922, 55, [B], 1006; *A.*, i, 582; A. Hantzsch, *ibid.*, 3180; *A.*, i, 1177.

<sup>54</sup> A. v. Baeyer and Oeconomides, *ibid.*, 1882, 15, 2093; *A.*, 1883, 201.

<sup>55</sup> A. Hantzsch, *ibid.*, G. Heller, *ibid.*, 2681; *A.*, i, 1058; compare *Ann. Reports*, 1921, 17, 116.

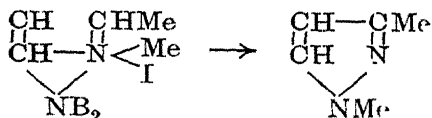


*Stereoisomerism.*

Although there has been no novel development in the stereochemistry of heterocyclic compounds during the period under review, a number of interesting applications have been made of known principles. Besides those already referred to, they are mentioned in connexion with catechin (p. 146), picrorocellin (p. 151), bishydrocarbostyryl-3 : 3'-spiran (p. 152), quinine (p. 157), anhydroecgonine (p. 160), and scopolamine (p. 161).

*Alkylation.*

The sodium salt of 5-chloro-3-methylpyrazole gives rise to 3-chloro-1 : 5-dialkyl derivatives.<sup>56</sup> This result is the more interesting since 1 : 5-dialkylpyrazoles themselves seem incapable of existence. Thus, alkylation of 3-alkylpyrazoles furnishes a 1 : 3-, but no 1 : 5-derivative. All attempts to synthesise the latter have failed, and even when 1 : 5-dimethylpyrazoline is oxidised, 1 : 3-dimethylpyrazole is formed. Similarly, although 1-phenyl-3-methylpyrazole methiodide is converted into 1-phenyl-3-methylpyrazole by heat, the corresponding 1-benzyl-compound yields 1 : 3-dimethylpyrazole under these conditions :<sup>57</sup>



The properties of the methylation product from the sodium salt of 5-chloro-3-phenylpyrazole differ from those attributed to either of the products which might have been expected.<sup>58</sup> The alkylation of 3-phenyl-5-pyrazolone has already been referred to.

Alkylation of 3-phenylindazole leads to results varying with the conditions employed, but there is a predominant tendency for the substituent to enter the 1-position.<sup>59</sup>

A new dimethyl derivative has been prepared by treating leuco-indigotin in persistently alkaline solution with methyl sulphate. This is considered to be an *O*-substituted compound, since it is converted by nitrous acid into indigotin, and by chromic acid into isatin.<sup>60</sup>

There are grounds for the belief that alkylation of the glyoxalines does not proceed by direct replacement of an imino-hydrogen

<sup>56</sup> C. A. Rojahn, *Ber.*, 1922, **55**, [B], 2959; *A.*, i, 1183.

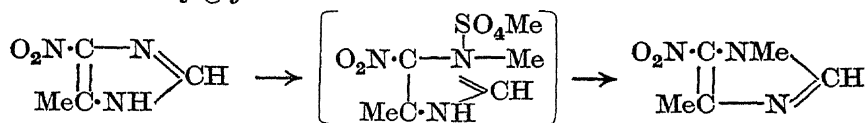
<sup>57</sup> K. v. Auwers and H. Broche, *ibid.*, 3880; *A.*, 1923, i, 151.

<sup>58</sup> C. A. Rojahn, *loc. cit.*

<sup>59</sup> K. v. Auwers and K. Hüttner, *Ber.*, 1922, **55**, [B], 112; *A.*, i, 682.

<sup>60</sup> E. Grandmougin, *Compt. rend.*, 1922, **174**, 758; *A.*, i, 470.

atom, and the following scheme is put forward for the case of 4-nitro-5-methylglyoxaline : <sup>61</sup>



A 1 : 3-dimethyl derivative is obtained by the action of diazomethane on uracil. <sup>62</sup>

#### *Five-membered Heterocyclic Structures.*

The formula of the elsholtzic acid derived from the action of amyl nitrite and sodium ethoxide on elsholtzione <sup>63</sup> has now been confirmed by its oxidation to furan-2 : 3-dicarboxylic acid. The constitution of this in turn is decided by its preparation from the chloride of synthetic <sup>64</sup> 2-methylfuran-3-carboxylic acid. Bromination of this compound occurs partly in the side chain and partly in the nucleus, so that hydrolysis of the product furnishes a bromo-2-hydroxymethylfuran-3-carboxylic acid. This undergoes oxidation to the corresponding dicarboxylic acid, from which the bromine is removed by means of zinc dust and ammonium chloride. <sup>65</sup>

The possibility of synthesising coumarins by condensation of phenol or their ethers with fumaric, maleic, or malic acid has been investigated, but with somewhat discordant results. <sup>66</sup>

A closer examination of the product of the action of acetylene on finely divided iron pyrites at 300° has shown that whilst thiophen constitutes 40 per cent. of the whole, it is accompanied by its 2- and 3-methyl and -ethyl derivatives, as well as by a number of other products, which do not contain sulphur. <sup>67</sup>

The resemblance between thiophen and benzene extends to their behaviour towards ethyl diazoacetate. In the former case, reaction only occurs at 130° in presence of an excess of thiophen. The product, obtained in poor yield, is probably ethyl *dicyclo*-Δ<sup>2</sup>-α-penthiophen-5-carboxylate,  $\begin{array}{c} \text{CH}-\text{CH} \\ \parallel \\ \text{CH}\cdot\text{S}\cdot\text{CH} \end{array} \text{>CH}\cdot\text{CO}_2\text{Et}$ , <sup>68</sup> since it

<sup>61</sup> F. L. Pyman, *T.*, 1922, 121, 2619.

<sup>62</sup> T. B. Johnson, A. J. Hill, and F. H. Case, *Proc. Nat. Acad. Sci.*, 1922, 8, 44; *A.*, i, 471.

<sup>63</sup> Compare *Ann. Reports*, 1920, 16, 114.

<sup>64</sup> E. Benary, *Ber.*, 1911, 44, 493; *A.*, 1911, i, 319.

<sup>65</sup> Y. Asahina and S. Kuwada, *J. Pharm. Soc. Japan*, 1922, 485, 565; *A.*, i, 1047.

<sup>66</sup> G. C. Bailey and F. Boettner, *J. Ind. Eng. Chem.*, 1921, 13, 905; *A.*, 1921, i, 879; W. Ponndorf, D.R.-P. 338737; *A.*, i, 565.

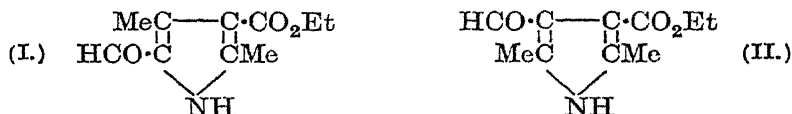
<sup>67</sup> W. Steinkopf and J. Herold, *Annalen*, 1922, 428, 123; *A.*, i, 850; compare W. Steinkopf, *Annalen*, 1914, 403, 11; *A.*, 1914, i, 425.

<sup>68</sup> W. S. Steinkopf and H. Augestad-Jensen, *ibid.*, 154; *A.*, i, 851.

easily forms an amide, and therefore probably contains a secondary rather than a tertiary carbon atom in the  $\alpha$ -position to the carbethoxy-group.<sup>69</sup>

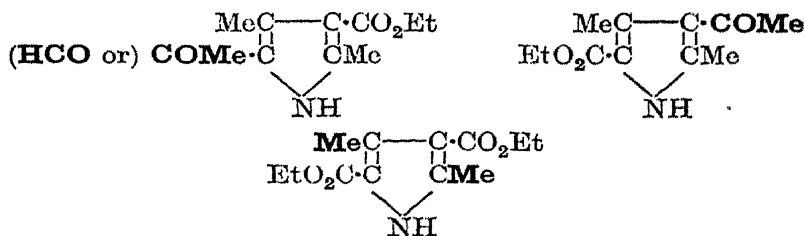
The catalytic reduction of pyrrole in presence of nickel at 200° results in the opening of the ring in every possible manner, since ammonia, diethylamine, methyl-*n*-propylamine, and *n*-butylamine are formed. The production of *n*-amylamine and ethyl-*n*-propylamine at the same time is attributed to the preliminary formation of piperidine through the intermediary of *N*-methylpyrrole.<sup>70</sup>

It has been shown<sup>71</sup> that the pyrrole nucleus is amenable to the Gattermann synthesis of aldehydes by means of hydrogen cyanide, and that, as the formulæ (I) and (II) show, substitution may occur in the  $\alpha$ - as well as in the  $\beta$ -position.



In view of this result, and the known similarity in reactivity between pyrrole and phenol, it is not surprising that the Hoesch synthesis also may be applied to pyrrole. The use of cyanogen or malononitrile in this connexion results in the formation of cyanoketones, and not of diketones.<sup>72</sup>

Not only acetyl or carboxyl,<sup>73</sup> but also methyl groups<sup>74</sup> are replaceable in the pyrrole nucleus by the nitro-group through the agency of nitric acid. The following formulæ, in which the groups which suffer replacement are indicated by heavy type, suggest that the order of replaceability is acetyl, methyl, and carbethoxyl :



The formula (III) is suggested for tripyrrole, from a determination

<sup>69</sup> Compare E. Fischer and W. Diltney, *Ber.*, 1902, **35**, 844; *A.*, 1902, **i**, 269.

<sup>70</sup> N. J. Putochin, *ibid.*, 1922, **55**, [B], 2742; *A.*, **i**, 1176.

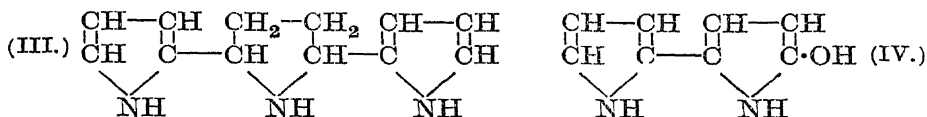
<sup>71</sup> H. Fischer and W. Zerweck, *ibid.*, 1942; *A.*, **i**, 758.

<sup>72</sup> H. Fischer, K. Schnelle, and W. Zerweck, *ibid.*, 2390; *A.*, **i**, 1055.

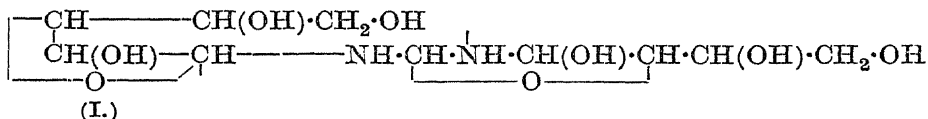
<sup>73</sup> G. Ciamician and H. Silber, *ibid.*, 1885, **18**, 1456; 1886, **19**, 1078; *A.*, 1885, 992; 1886, **i**, 718.

<sup>74</sup> H. Fischer and W. Zerweck, *ibid.*, 1922, **55**, [B], 1949; *A.*, **i**, 758.

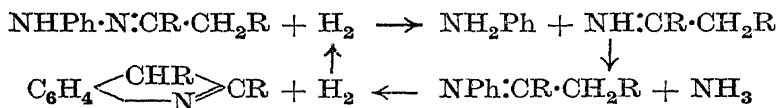
of the  $\alpha$ -positions available for coupling with diazomium compounds and the formation of succinic acid by oxidation with chromic acid. For similar reasons, hydroxydipyrrole is considered to be (IV) or the corresponding ketone.<sup>75</sup>



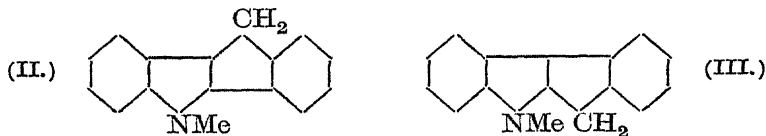
By distillation of chitin with zinc dust, a mixture of bases is obtained, which contains some pyridine derivatives, but consists chiefly of pyrroles. Of the latter, one appears to be identical with synthetic  $\alpha$ -methyl-*N*-*n*-hexylpyrrole, and in consequence it is suggested that the grouping (I) is present in chitin.<sup>76</sup>



In a review<sup>77</sup> of the various explanations which have been offered of the Fischer indole synthesis, preference is given to that which<sup>78</sup> postulates the intermediate formation of an anil :



In order to explain the extension of the reaction to phenylmethylhydrazones, it is assumed that the ketimine formed in the first stage of the reaction may react in the aminic form,  $\text{NH}_2\text{·CR:CHR}$ . Reference may be made here to the synthesis of the indenoindoles (II) and (III) by heating the phenylmethylhydrazones of  $\alpha$ - and  $\beta$ -hydrindones, respectively, with concentrated hydrochloric acid.<sup>79</sup>



The pyrogenetic synthesis of indole by passing a mixture of

<sup>75</sup> A. Pieroni and A. Moggi, *Atti R. Accad. Lincei*, 1922, [v], 31, i, 381; *A.*, i, 766.

<sup>76</sup> P. Karrer and A. P. Smirnoff, *Helv. Chim. Acta*, 1922, 5, 832; *A.*, 1923, i, 122.

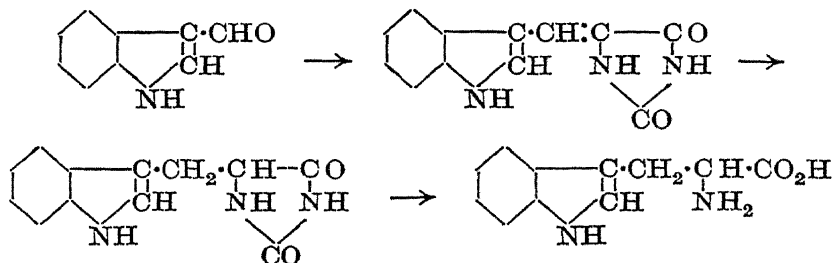
<sup>77</sup> C. Hollins, *J. Amer. Chem. Soc.*, 1922, 44, 1598; *A.*, i, 863.

<sup>78</sup> G. Reddelien, *Annalen*, 1912, 388, 179; *A.*, 1912, i, 363.

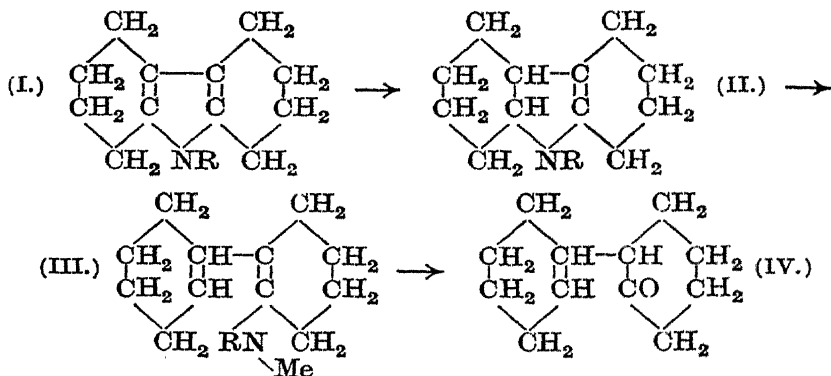
<sup>79</sup> J. W. Armit and R. Robinson, *T.*, 1922, 121, 827.

aniline vapour, acetylene, and carbon dioxide through an iron tube at  $700^{\circ}$  is moderately successful. A quantity of crude indole was collected amounting, in the most favourable case,<sup>80</sup> to 34 per cent. by weight of the aniline not recovered.

A new synthesis of *r*-tryptophan has been described. Indole is successively converted into magnesium  $\beta$ -indolyl bromide, and  $\beta$ -aldehydoindole, which is then condensed with hydantoin by the Perkin reaction to  $\beta$ -indolaldehydantoin. Reduction with sodium amalgam, followed by hydrolysis, completes the synthesis :<sup>81</sup>



The catalytic reduction of *N*-methyl- or -ethyl-carbazole in presence of nickel salts at  $215^{\circ}$  under pressure and in absence of a solvent furnishes, besides unchanged material, a mixture of the tetrahydro-derivative, insoluble in acid, and the basic octahydro-derivative (I), from which a decahydro-derivative (II) is obtained by the action of tin and hydrochloric acid. The constitution of the deoxy-base (III), derived from this, follows from its hydrolysis by acids to 2- $\Delta^1$ -cyclohexenylcyclohexanone (IV) :<sup>82</sup>



The result is of interest as indicating that the formation of pyrrolines (corresponding with II) from pyrroles proceeds simply by the

<sup>80</sup> R. Majima, T. Unno, and K. Ono, *Ber.*, 1922, **55**, [B], 3854; *A.*, 1923, i, 135.

<sup>81</sup> R. Majima and M. Kotake, *ibid.*, 3859; *A.*, 1923, i, 156.

<sup>82</sup> J. v. Braun and H. Ritter, *ibid.*, 3792; *A.*, 1923, i, 141.

reduction of one double bond rather than by reduction of the conjugated system, followed by isomerisation.

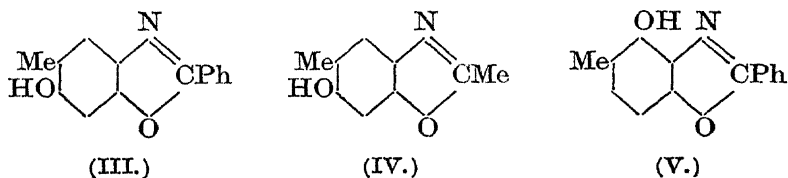
The formation of indigotin by alkaline fusion of dianilidofumaric acid, from aniline and dibromofumaric acid, has been described.<sup>83</sup>

6 : 6'-Dibromindigotin has been isolated from the fluid expressed from certain varieties of cockle, which the natives of Mexico have long utilised for dyeing purposes.<sup>84</sup>

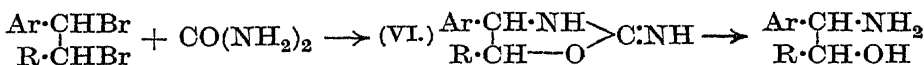
Formulae reminiscent of the indigoid type have been assigned to the product (I) of the oxidation of rhodanine by ferric chloride,<sup>85</sup> and, provisionally, to "naphthothiam blue," (II) the leuco-compound of which is formed when 1 : 8-nitronaphthalenesulphinic acid is reduced with zinc dust and potassium sulphite.<sup>86</sup>



In accordance with the relationship, previously noticed, between the constitution of benzoxazole derivatives and their capacity for visible fluorescence,<sup>87</sup> (III) exhibits this property, but (IV) and (V) do not.<sup>88</sup>



Imino-oxazolidines (VI) result from the condensation of styrene dibromides with carbamide :



Their hydrolysis with alkali hydroxides provides a new method for the preparation of alkamines.<sup>89</sup>

<sup>83</sup> G. C. Bailey and R. S. Potter, *J. Amer. Chem. Soc.*, 1922, **44**, 215; *A.*, i, 370.

<sup>84</sup> P. Friedlaender, *Ber.*, 1922, **55**, [B], 1655; *A.*, i, 793.

<sup>85</sup> C. Gränacher, H. Reis, and E. Pool, *Helv. Chim. Acta*, 1922, **5**, 382; *A.*, i, 576.

<sup>86</sup> A. Reissert, *Ber.*, 1922, **55**, [B], 858; *A.*, i, 583.

<sup>87</sup> Compare *Ann. Reports*, 1921, **18**, 127.

<sup>88</sup> F. Henrich, H. Suntheimer, and C. Steinmann, *Ber.*, 1922, **55**, [B], 3911; *A.*, 1923, i, 145.

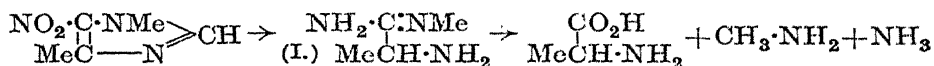
<sup>89</sup> J. Takeda and S. Kuroda, *J. Pharm. Soc. Japan*, 1919, **449**, 561; 1921, 1; *A.*, 1920, i, 228; 1922, i, 272.

The evidence of the non-existence of 1 : 5-dialkylpyrazoles has already been summarised (p. 136). This forms a basis for an adverse criticism of Knorr's view that one hydrogen atom in the pyrazole nucleus is oscillatory and it is suggested that the cause of the apparent identity of 3- and 5-derivatives of pyrazole, on which this view is based, is again the instability of one form, and its consequent transition to the other.<sup>90</sup>

A study of the electrochemical oxidation of pyrazoles has shown that, in acid suspension, the heterocyclic nucleus of 1-phenyl-3-methylpyrazole is destroyed, but that in presence of potassium carbonate solution, the benzene nucleus is destroyed, with formation of pyrazole-3-carboxylic acid.<sup>91</sup>

The applicability of the Friedel-Crafts reaction to 5-chloropyrazoles, giving rise to substitution in the 4-position, is limited to 1-aryl derivatives and to the chlorides of aromatic acids.<sup>92</sup>

The difficulty associated with the original explanation of the behaviour of the 5-nitroglyoxalines on reduction was indicated in a previous Report.<sup>93</sup> *dl*-Alanine-*N*-methyramidine (I) has since been found among the reduction products of 5-nitro-1 : 4-dimethylglyoxaline (prepared by nitration of 1 : 4-dimethylglyoxaline). Accordingly, the reaction is now considered to be analogous to the rupture of the glyoxaline ring by means of benzoyl chloride and sodium hydroxide, and in the case referred to is represented as follows :



4-Nitro-1 : 5-dimethylglyoxaline, from the nitration of 1 : 5-dimethylglyoxaline, yielded the amino-compound, with *dl*-*N*-methylalanine and ammonia.<sup>94</sup> These results confirm the orientations provisionally adopted<sup>95</sup> for the above two dimethyl derivatives, when they were prepared from 4-methylglyoxaline, and also the suggestion that pilocarpine is a 1 : 5-derivative of glyoxaline. Considerations of space prevent more than a reference to the discussion of the behaviour of the glyoxalines on alkylation (compare p. 136) and towards benzoyl chloride and sodium hydroxide from the point of view of polarity. The inadequacy of earlier suggestions in regard to the latter reaction is indicated in a review

<sup>90</sup> K. v. Auwers and H. Broche, *Ber.*, 1922, 55, [B], 3880; *A.*, 1923, i, 151.

<sup>91</sup> Fr. Fichter and H. de Montmollin, *Helv. Chim. Acta*, 1922, 5, 256; *A.*, i, 470.

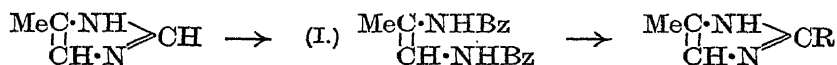
<sup>92</sup> O. A. Rojahn, *Ber.*, 1922, 55, [B], 291; *A.*, i, 373.

<sup>93</sup> *Ann. Reports*, 1920, 17, 115.

<sup>94</sup> F. L. Pyman, *T.*, 1922, 121, 2616.

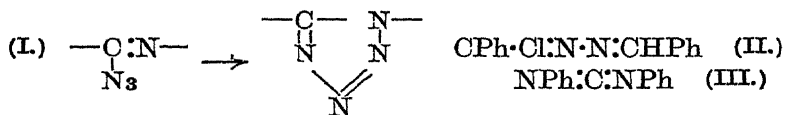
<sup>95</sup> *Idem*, *ibid.*, 1910, 97, 1814.

of this,<sup>96</sup> in which it is shown that the ring may also be opened by means of *isovaleryl chloride*. Neither benzenesulphonyl chloride nor acetic anhydride, however, is effective. The result in the last case is the more striking, since the same reagent opens the benzoglyoxaline ring,<sup>97</sup> and yet the latter is the more resistant towards benzoyl chloride and pyridine. These reactions permit the conversion of glyoxalines into 2-alkyl derivatives, since it has been shown<sup>98</sup> that when, for example, bisbenzoylaminopropylene (I), derived from 5-methylglyoxaline, is heated with the anhydride of an aliphatic acid, 2-alkyl-5-methylglyoxaline is produced :

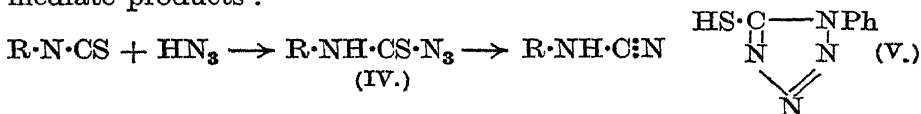


The polybromo-compounds resulting from the direct halogenation of glyoxalines may be converted into monobromo-derivatives by treatment with sodium sulphite solution.<sup>99</sup>

The rearrangement of the system (I) in certain compounds to furnish 1 : 2 : 3 : 4-tetrazoles would appear to be an intramolecular reaction comparable with the familiar intermolecular saturation of a double bond by the action of diazo-compounds :



Suitable azides of the type (I) are generated as intermediate products (not isolated) by interaction of sodium azide and benzylidenebenzhydrazide chloride (II) or carbodiphenyldi-imide (III), or, in place of the latter, a mixture of a thiourea or a thiosemicarbazide with lead oxide.<sup>1</sup> Again, when mustard oils are heated with azoimide in an indifferent solvent, cyanamides are formed as intermediate products :



<sup>96</sup> A. Windaus, W. Dörries, and H. Jenssen, *Ber.*, 1921, 54, [B], 2745; *A.*, i, 60.

<sup>97</sup> G. Heller, *ibid.*, 1904, 37, 3115; *A.*, 1904, i, 942.

<sup>98</sup> A. Windaus and W. Langenbeck, *ibid.*, 1922, 55, [B], 3706; *A.*, 1923, i, 147.

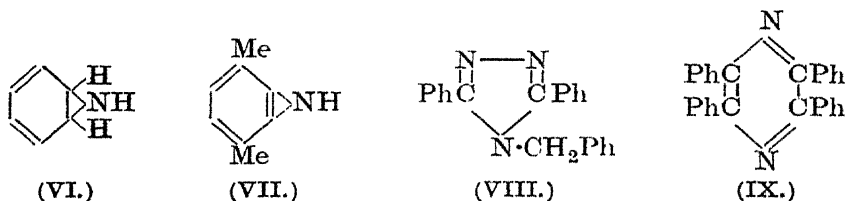
<sup>99</sup> I. E. Balaban and F. L. Pyman, *T.*, 1922, 121, 947; L. Light and F. L. Pyman, *ibid.*, 2626.

<sup>1</sup> R. Stollé, *Ber.*, 1922, 55, [B], 1289; R. Stollé and A. Netz, *ibid.*, 1297; *A.*, i, 689, 690.

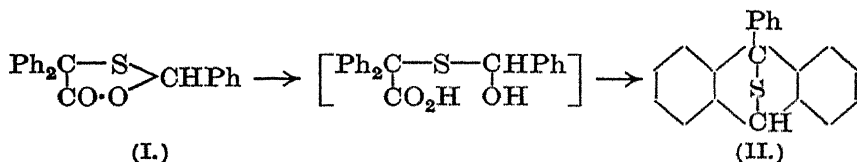


These then react with more azimide to form tetrazoles. 5-Mer-capto-1-phenyl-1:2:3:4-tetrazole (V) is formed when phenyl-carbimide is boiled with an alcoholic suspension of sodium azide, or when the corresponding thiocarbamic azide (type IV) is treated with alkali.<sup>2</sup>

$\psi$ -Aniline (VI) is the sole product of the interaction of sulphuryl azide,  $\text{SO}_2(\text{N}_3)_2$ , and benzene at  $140^\circ$ ,<sup>3</sup> but from *p*-xylene, a mixture of  $\psi$ -*p*-xylidine with a base, possibly (VII), and a solid of the same composition, are formed.<sup>4</sup> The products obtained when benzyl azide is heated with *p*-xylene, on the other hand, are entirely derived from the azide, and include (VIII) and (IX):<sup>5</sup>



The interaction of thiobenzilic acid and benzaldehyde in presence of hydrogen chloride leads to the formation of triphenyl-1:3-oxthiophan-5-one (I). This, on treatment with cold concentrated sulphuric acid, yields a product, to which the formula (II) is assigned on the grounds of its conversion into 9-phenylanthracene by distillation with zinc dust, and of its insolubility in alkali.<sup>6</sup>



### The Pyrone Group.

The method whereby pyrylium salts are synthesised by condensation of an *o*-hydroxybenzaldehyde with a compound containing the  $\cdot\text{CH}_2\cdot\text{CO}\cdot$  group<sup>7</sup> has been shown<sup>8</sup> to be applicable

<sup>2</sup> E. Oliveri-Mandalà, *Gazzetta*, 1921, 51, ii, 195; 1922, 52, i, 101; *A.*, 1921, i, 900; 1922, i, 473.

<sup>3</sup> F. Schmidt, *Ber.*, 1922, 55, [B], 1581; *A.*, i, 777.

<sup>4</sup> T. Curtius and F. Schmidt, *ibid.*, 1571; *A.*, i, 776.

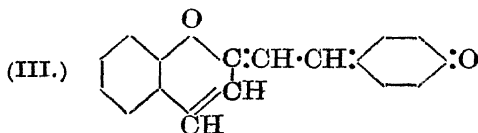
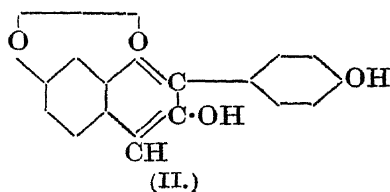
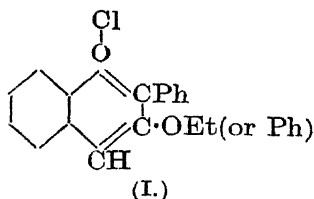
<sup>5</sup> T. Curtius and G. Ehrhardt, *ibid.*, 1559; *A.*, i, 775.

<sup>6</sup> A. Bistrzycki and B. Brenken, *Helv. Chim. Acta*, 1922, 5, 20; *A.*, i, 268.

<sup>7</sup> W. H. Perkin and R. Robinson, *P.*, 1907, 19, 149; H. Decker and T. v. Fellenberg, *Ber.*, 1907, 40, 3815; *Annalen*, 1907, 356, 281; *A.*, 1907, i, 950.

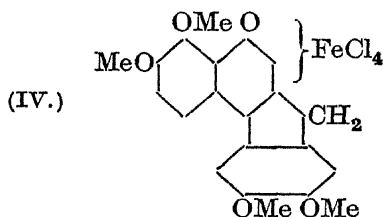
<sup>8</sup> D. D. Pratt and R. Robinson, *T.*, 1922, 121, 1577.

to  $\omega$ -ethoxy- and -phenoxy-acetophenones, yielding compounds (I) of the anthocyanidin type.



The blue anthocyanidin pigments have been considered to be alkali salts of phenol betaines, for example (II). This view has, however, been criticised<sup>9</sup> on the ground that it cannot be applied to the colour change of solutions of 4'-hydroxy-2-styrylbenzopyrylium chloride from red to blue on dilution with water, in absence of any base. The change is attributed to production of the quinonoid compound (or, less probably, a corresponding betaine) (III). The pyrylium compound in question is synthesised by the action of hydrogen chloride on a solution of *o*-hydroxy-styryl methyl ketone and *p*-hydroxybenzaldehyde in formic acid.

A synthesis of *isohæmatein* tetramethyl ether ferrichloride (IV) has been carried out<sup>10</sup> by reactions precisely analogous to those used in the case of *isobrazilein* trimethyl ether.<sup>11</sup>



Demethylation of the above ferrichloride by means of hydrochloric acid furnished a product identical with the *isohæmatein* from hæmatoxylin.<sup>12</sup>

No definite conclusion has yet been reached in the controversy<sup>13</sup>

<sup>9</sup> J. S. Buck and I. M. Heilbron, *T.*, 1922, **121**, 1198.

<sup>10</sup> H. G. Crabtree and R. Robinson, *ibid.*, 1033.

<sup>11</sup> Compare *Ann. Reports*, 1918, **15**, 104.

<sup>12</sup> J. J. Hummel and A. G. Perkin, *T.*, 1882, **41**, 373.

<sup>13</sup> *Ann. Reports*, 1920, **17**, 110; 1921, **18**, 129; A. C. von Euler, *Svensk. Kem. Tidskr.*, 1921, **33**, 88; *A.*, i, 45.

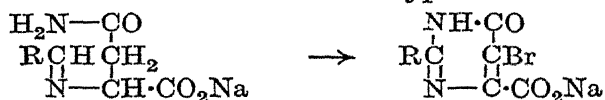
regarding the constitution of catechin. The crystallographic evidence in favour of a formula of the  $\alpha\gamma$ -diphenylpropane type has been met with equally definite evidence of the same character in favour of the  $\alpha\alpha$ -type of formula.<sup>14</sup> An intimation<sup>15</sup> that the discrepancies are to be subjected to independent investigation is therefore to be welcomed. In this paper, the optical activity of acacatechin is denied. On the other hand, the optical activity of the pentacetyl derivatives of three samples of catechin has been independently affirmed,<sup>16</sup> and evidence of a somewhat ingenious type is also offered of the presence of two asymmetric carbon atoms in the catechin molecule. In the course of the latter investigation, *dl*-epicatechin was prepared, and then detected in Pegu-catechu.<sup>17</sup>

#### *The Pyrimidines.*

Two new syntheses of pyrimidine derivatives have been recorded. Mono- and di-alkylmalonic esters condense with aromatic amidines in presence of sodium ethoxide, yielding respectively insoluble yellow (I), and soluble colourless derivatives (II):<sup>18</sup>

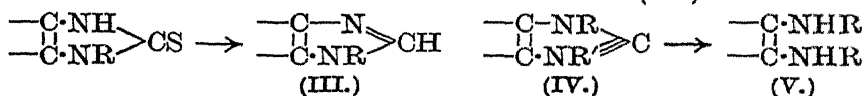


The condensation products of aldehydes with asparagine furnish good yields of hydroxybromopyrimidinecarboxylic acids on oxidation with alkaline solutions of sodium hypobromite:



The unbrominated compounds may be obtained by use of potassium permanganate, but the yields are not so good. The presence of asparagine in young etiolated shoots has prompted the suggestion that a reaction similar to these may produce the pyrimidines and purine bases found in nucleoproteins.<sup>19</sup>

The desulphurisation of 9-alkyl-8-thiouric acids by treatment with nitrous acid leads to the formation of xanthines (III):



<sup>14</sup> M. Nierenstein, *T.*, 1922, 121, 604.

<sup>15</sup> M. Nierenstein, *Ber.*, 1922, 55, [B], 3831.

<sup>16</sup> K. Feist and A. Futtremenger, *ibid.*, 942; *A.*, i, 565.

<sup>17</sup> K. Freudenberg, O. Böhme, and L. Purrmann, *ibid.*, 1734; *A.*, i, 756; K. Freudenberg, *ibid.*, 1938; *A.*, i, 756.

<sup>18</sup> A. W. Dox and L. Yoder, *J. Amer. Chem. Soc.*, 1922, 44, 311; *A.*, i, 374.

<sup>19</sup> E. Cherbuliez and K. N. Stavritch, *Helv. Chim. Acta*, 1922, 5, 267; *A.*, i, 581.

When the reaction is extended to 7:9-dialkyl-8-thiouric acids, sulphur is again removed, but the alkyl groups and the pyrimidine ring remain intact. In accordance with the formula (IV) assigned to the resulting deoxyuric acids, acid hydrolysis gives rise to dialkyluracils (V), the monoformyl derivatives of which are obtained by alkaline hydrolysis.<sup>20</sup>

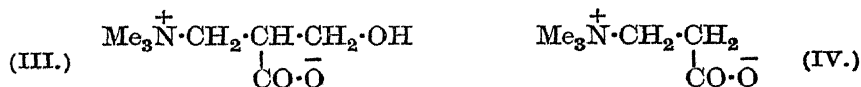
### Betaines.

The discordance between the ordinary formulæ for the various types of betaines, including certain dyestuffs like gallocyanine, rosindone, and cyanidine, and the usual stereochemical conceptions is well known. It has now been suggested<sup>21</sup> that the betaine structure is not cyclic in the ordinary sense, but represents a dipolar unit, for example (I),



containing within itself the opposite charges carried by the sodium and chlorine ions in solid sodium chloride. The analogy supplies an explanation of the high melting point and the low solubility in organic solvents which characterise the amino-acids and betaines.<sup>22</sup> In further confirmation of this view, it has been shown that a betaine results from the hydrolysis of the quaternary methiodide of methyl *trans-p*-dimethylaminocinnamate (II).<sup>23</sup> Similarly, the salts of dibasic acids with multivalent metals are to be compared with calcium carbonate.

Carnitine is now considered to be a  $\beta$ -betaine (III), since it shows the behaviour of a  $\beta$ -hydroxy-acid, in that it suffers dehydration to *apocarnitine* by concentrated sulphuric acid at 130°.<sup>24</sup> This reaction distinguishes carnitine from the synthetic product,<sup>25</sup> with which it had previously been thought identical. The formula also explains the formation of  $\beta$ -bromobetaine (IV) from carnitine on oxidation.<sup>26</sup>



Apophyllenic acid is probably a 4- (I) rather than a 3-betaine,

<sup>20</sup> H. Biltz and others, *Annalen*, 1922, **426**, 237—299; *A.*, i, 380—384.

<sup>21</sup> P. Pfeiffer, *Ber.*, 1922, **55**, [B], 1762; *A.*, i, 720.

<sup>22</sup> Compare A. Reis, *Z. Physik*, 1920, **1**, 204; *A.*, 1920, ii, 537.

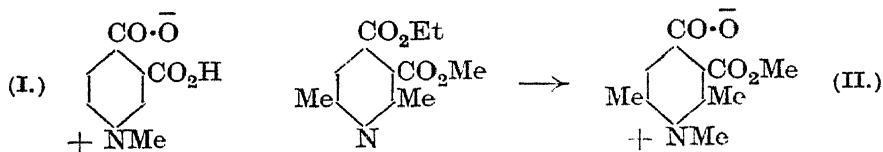
<sup>23</sup> P. Pfeiffer and G. Haefelin, *Ber.*, 1922, **55**, [B], 1769; *A.*, i, 738.

<sup>24</sup> R. Engeland, *ibid.*, 1921, **54**, [B], 2208; *A.*, 1921, i, 880.

<sup>25</sup> E. Fischer and A. Göddertz, *ibid.*, 1911, **44**, 3279; *A.*, 1911, i, 19.

<sup>26</sup> R. Engeland, *ibid.*, 1909, **42**, 2457; *A.*, 1909, i, 551.

since synthetic 3-methyl 4-ethyl 2 : 6-dimethyleinchomeronate<sup>27</sup> is converted by treatment with methyl iodide and moist silver oxide into methyl, not ethyl, 2 : 6-dimethylapophyllenate (II) :

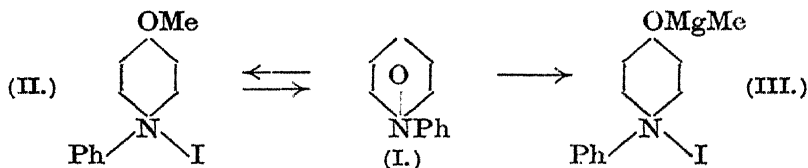


The new betaine notation furnishes a possible explanation of the apparent anomaly that silver apophyllenate is not converted by methyl iodide into methyl apophyllenate, but into the isomeric betaine.<sup>28</sup>

### *The Pyridine Group.*

Attention may be directed to a discussion of the separation of pyridine, and its methyl and dimethyl derivatives from coal tar oil in a state of purity.<sup>29</sup>

A formula of the type (I) is suggested<sup>30</sup> in place of the usual ketonic formula for the  $\gamma$ -pyridones, on the ground that these do not show ketonic reactions and are colourless. Although an additive compound (II) of



of *N*-phenylpyridone with methyl iodide may be prepared,<sup>31</sup> its properties are not those of a true ammonium iodide, since the corresponding hydroxide reverts to the pyridone when its solution is evaporated, as does the additive compound of the pyridone with magnesium methyl iodide (III) when treated with acid. Further, the changes observable during the course of the reaction between chelidonic acid and amines suggest that this occurs in three stages, which are thus represented :

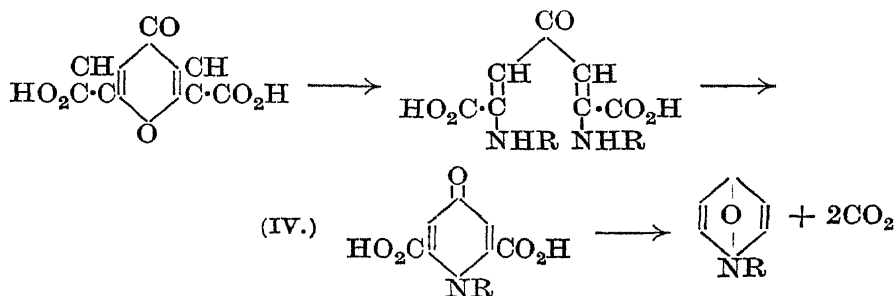
<sup>27</sup> Compare *Ann. Reports*, 1918, 15, 101.

<sup>28</sup> O. Mumm and E. Gottschaldt, *Ber.*, 1922, 55, [B], 2064, 2075; *A.*, i, 861, 862.

<sup>29</sup> J. G. Heap, W. J. Jones, and J. B. Speakman, *J. Amer. Chem. Soc.*, 1921, 43, 1936; *A.*, i, 171.

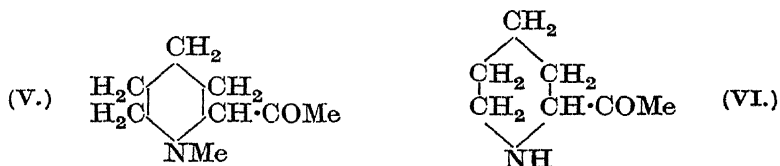
<sup>30</sup> A. P. Smirnoff, *Helv. Chim. Acta*, 1921, 4, 599; *A.*, 1921, i, 594; *Ber.*, 1922, 55, [B], 612; *A.*, i, 464.

<sup>31</sup> W. Borsche and I. Bonacker, *Ber.*, 1921, 54, [B], 2678; *A.*, i, 50.



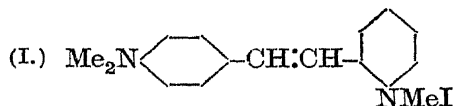
In the first, at the ordinary temperature the pyrone ring is opened. In the second, a homogeneous coloured fluid melt is produced, which in the third stage passes into the colourless final product. Corresponding with (IV), a yellow *p*-tolyl derivative was isolated, and shown to furnish a phenylhydrazone.

A comparison of the ketone (V), synthesised in the usual manner,<sup>32</sup> with the corresponding ethyl ketones, *N*-methyl-conhydrinone and -isopelletierin, has shown that it resembles the latter rather than the former in its ready semicarbazone formation, but that its carbonyl group is not so easily reduced to a methylene group as



that of either of the others. All attempts, whether by direct or by indirect demethylation, to prepare piperidylethanone (VI) were unsuccessful.

The condensation of  $\alpha$ -picoline methiodide with *p*-dimethylamino-benzaldehyde results in the formation of a product (I), which constitutes the most powerful sensitiser yet known for green light for gelatino-silver bromide photographic plates.<sup>33</sup>



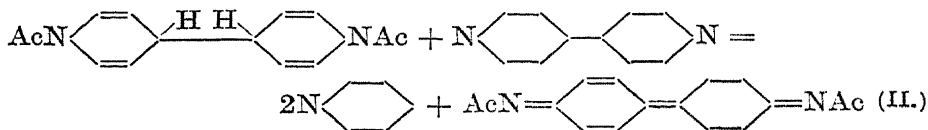
Interpretations of the reactions ensuing on the partial reduction of the pyridine nucleus<sup>34</sup> have been considerably revised, as a result of parallel investigations. Of these, perhaps the most illuminating are those concerned with the formation and reactions

<sup>32</sup> K. Hess and W. Corleis, *Ber.*, 1921, **54**, [B], 3010; *A.*, i, 170.

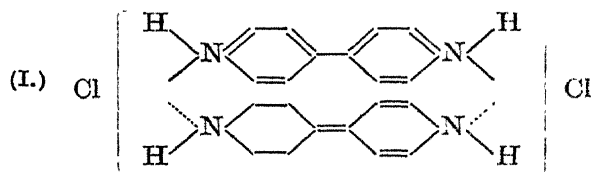
<sup>33</sup> W. H. Mills and (Sir) W. J. Pope, *T.*, 1922, **121**, 946.

<sup>34</sup> Compare *Ann. Reports*, 1920, **17**, 106; 1921, **18**, 134.

of diacetyltetrahydrodipyridyl.<sup>35</sup> This colourless compound, when prepared from pyridine, is accompanied by a small proportion of an orange product, identified as diacetyldihydrodipyridyl (II). This is easily oxidised by air or by bromine to  $\gamma\gamma$ -dipyridyl, or its perbromide, respectively, and may be obtained by adding acetic anhydride to the blue solution produced when dipyridyl is reduced by zinc dust and acetic acid.<sup>36</sup> It seems not to be directly obtainable from the tetrahydro-derivative, but is produced when this is heated with dipyridyl in acetic anhydride solution at 100°:



The significance of this lies in the fact that hot solutions of the tetrahydro-compound become blue only in presence of air (which is known to produce dipyridyl), or on the addition of dipyridyl. The blue colour therefore appears to be associated with the presence in solution of dihydrodipyridyl or a derivative. This inference is confirmed by the composition of "dipyridyl violet chloride" (I), prepared by reduction of dipyridyl with one equivalent of chromous chloride in presence of calcium chloride:



It will be noted that this compound differs from most quinhydrones in that the quinonoid portion is the reduced part of the molecule, and becomes aromatic by oxidation.

It has been recognised that the blue solutions obtained from the brown "benzoylpyridinium," yellow dimethyl- and diethyl-"tetrahydrodipyridyls," and red "benzoylpyridinium," most probably owe their origin to similar reactions. The last compound has been definitely recognised as *NN*-dibenzylldihydro- $\gamma\gamma$ -dipyridyl, but an account of this work is unnecessary, since in many respects the results are analogous to those just detailed. The obvious inference from the above that hydrogen atoms in the  $\gamma$ -position of the pyridine nuclei of the parent compounds are essential to

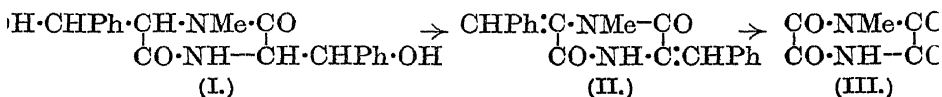
<sup>35</sup> O. Dimroth and F. Frister, *Ber.*, 1922, **55**, [B], 1223, 3693; *A.*, i, 678.

<sup>36</sup> The earlier statement, that the tetrahydro-compound is formed by this reaction, has been withdrawn; *loc. cit.*, 1223, footnote 2.

the production of blue solutions has been confirmed by an examination of the corresponding  $\gamma\gamma$ -dicollidyl and di-2 : 4-lutidyl compounds.<sup>37</sup>

### *Picrorocellin.*

Picrorocellin is the colourless mono-*O*-ether of 2 : 5-diketo-3 : 6-di- $\omega$ -hydroxybenzyl-1-methylpiperazine (I),<sup>38</sup> since on treatment with hydrochloric and acetic acids, it is converted into pale yellow xanthorocellin (II). The constitution of this product follows from its oxidation to benzaldehyde (and benzoic acid), and 2 : 3 : 5 : 6-tetraketo-1-methylhexahydro-1 : 4-diazine (III), identical with the compound<sup>39</sup> prepared by condensation of methyloxamide and oxalyl chloride. Since, further, methylation of the secondary amino- and the free hydroxyl groups of picrorocellin yields an internally compensated product, it follows that this, and hence probably also picrorocellin itself, has a *trans*-configuration.



### *The Quinoline Group.*

Quinoline and its derivatives rapidly absorb four atomic proportions of hydrogen in their pyridine nuclei, when they are reduced in presence of nickel salts under pressure, but the subsequent stages of reduction to decahydro-derivatives proceed much more slowly.<sup>40</sup>

The synthesis of cinchonic and quinic acids has continued to engage attention. The preparation of cinchonic acid by decomposition of the quinoline-2 : 4-dicarboxylic acid<sup>41</sup> resulting from the condensation of pyruvic acid with isatin has been extended to 6-methoxyisatin for the purpose of preparing quinic acid.<sup>42</sup> But the process would not seem to be as convenient as that in which 6-methoxyquinoline serves as a starting material.<sup>43</sup> Another process is outlined in the following scheme :

<sup>37</sup> B. Emmert and others, *Ber.*, 1921, 54, [B], 3168; 1922, 55, [B], 1352, 2322; E. Weitz and others, *ibid.*, 395, 599, 2864; *A.*, i, 179, 680, 1064, 365, 470, 1186.

<sup>38</sup> M. O. Forster and W. B. Saville, *T.*, 1922, 121, 816.

<sup>39</sup> J. V. Dubsky, *Ber.*, 1919, 52, 216; *A.*, 1919, i, 288.

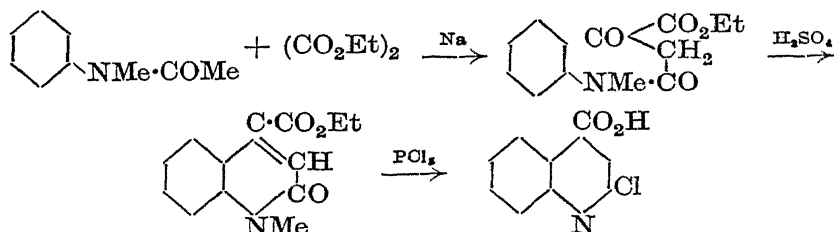
<sup>40</sup> J. v. Braun, A. Petzold, and J. Seeman, *ibid.*, 1922, 55, [B], 3779; *A.*, 1923, i, 136.

<sup>41</sup> W. Pfitzinger, *J. pr. Chem.*, 1902, [ii], 66, 263; *A.*, 1903, i, 53.

<sup>42</sup> J. Halberkann, *Ber.*, 1921, 54, [B], 3079; *A.*, i, 172.

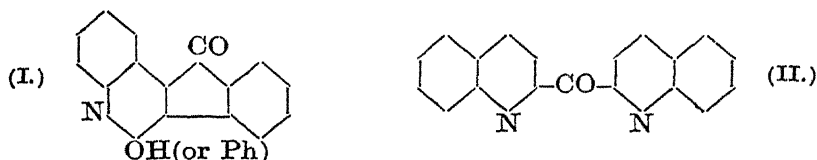
<sup>43</sup> A. Kaufmann, *ibid.*, 1922, 55, [B], 614; *A.*, i, 464.





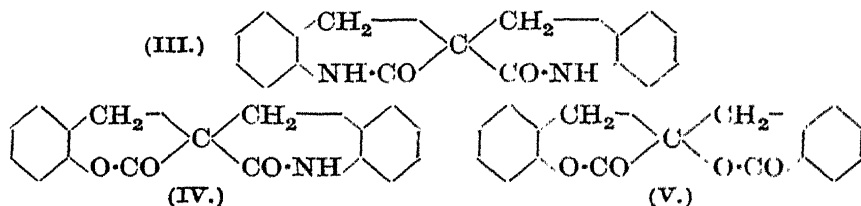
In this case the elimination of the halogen atom remains to be accomplished.<sup>44</sup>

The 2-hydroxy- and 2-phenyl-derivatives of 3-phenylcinchoninic acid undergo internal condensation when treated with sulphuric acid.<sup>45</sup>



As would be expected by analogy with fluorenone, the resulting ketones (I) are yellow, whilst di-2-quinolyl ketone (II), prepared by hydrolysis of the condensation product of nitrosodimethylaniline with diquinolylmethane, is colourless.<sup>46</sup>

Reduction of ethyl 2 : 2'-dinitrodibenzylmalonate furnishes bis-hydrocarbostyryl-3 : 3'-spiran (III), which is interesting owing to the asymmetry of its molecular structure :



Accordingly, its 6 : 6'-disulphonic acid has been resolved into optically active components by means of the quinine salts. The *spiro*-compounds (IV) and (V) were also prepared in the course of this investigation.<sup>47</sup>

The constitution previously attributed to the cyanines<sup>48</sup> has

<sup>44</sup> E. Thielepape, *Ber.*, 1922, 55, [B], 127; *A.*, i, 271.

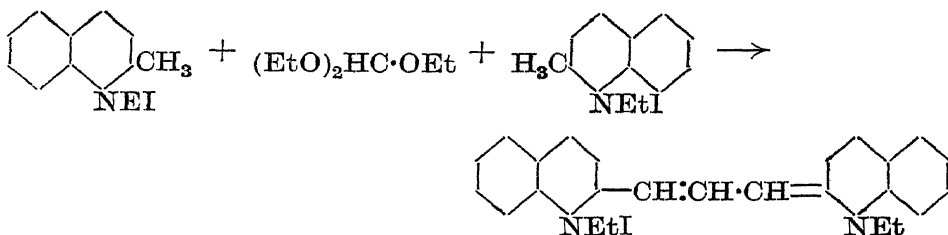
<sup>45</sup> Farb. vorm. Meister, Lucius, & Brüning, *D.R.-P.* 343322; *A.*, i, 867.

<sup>46</sup> G. Scheibe and G. Schmidt, *Ber.*, 1922, 55, [B], 3157; *A.*, i, 1190.

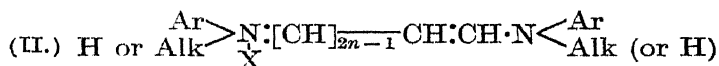
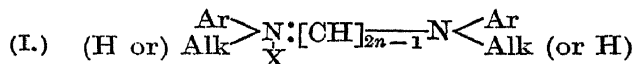
<sup>47</sup> H. Leuchs and H. v. Katinszky, *ibid.*, 710; H. Leuchs, (Miss) E. Conrad, and H. v. Katinszky, *ibid.*, 2131; *A.*, i, 471, 873.

<sup>48</sup> Compare *Ann. Reports*, 1920, 17, 121.

been confirmed by a synthesis of pinacyanol from quinaldine ethiodide and ethyl orthoformate in presence of acetic anhydride or zinc chloride :



This reaction, it may be noted, is common to the benzothiazoles and to the dialkylindolenines,<sup>49</sup> in which the  $\cdot\text{CH}:\text{CH}\cdot$  group of the quinoline nucleus is replaced respectively by  $:\text{S}$  and  $:\text{CR}_2$ . Further, it has been shown that the absorption curves, whether in neutral or in acid solution, of pinacyanol and of diethylisocyanine are almost identical in form. This is a particular case of a valuable generalisation that the absorption curves of compounds, the relationship of which is expressed by the formulæ (I) and (II), are very similar, to an extent increasing with the value of  $n$ .



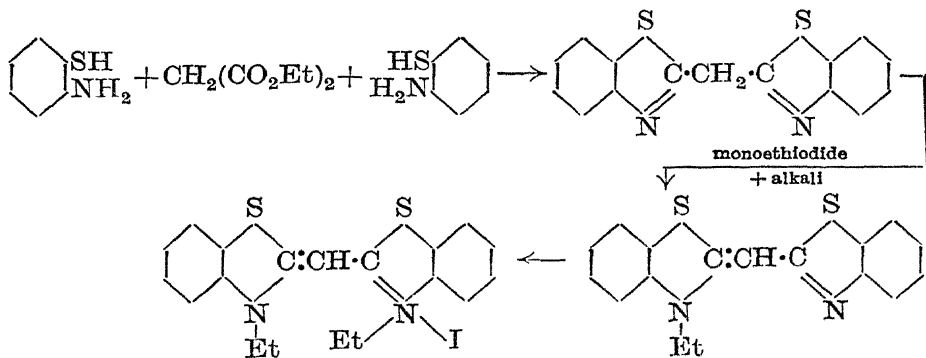
The same paper<sup>50</sup> contains a general review of the various types of cyanines, and proposals for a comprehensive system of nomenclature to replace the present somewhat trivial designations, and capable of application to products in which the unsaturated carbon chain between the nuclei is prolonged. Compounds of this type have yet to be prepared, but experiments in this direction will not be lacking in view of the obvious interest attaching to them.

The two dyestuffs, which result from the action of a base, preferably pyridine, on a mixture of the alkyl iodides of benzothiazole and its 1-methyl derivative, correspond in general properties to the cyanines.<sup>51</sup> This similarity extends to their constitution, for the yellow diethylthiocyanine iodide has been synthesised by the reactions indicated :

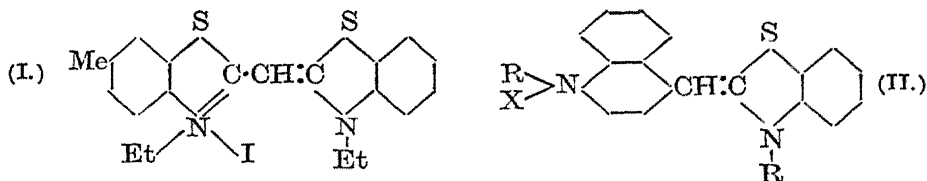
<sup>49</sup> Compare W. König, *J. pr. Chem.*, 1911, [ii], 84, 194; *A.*, 1911, i, 808.

<sup>50</sup> W. König, *Ber.*, 1922, 55, [B], 3293; *A.*, i, 1188.

<sup>51</sup> A. W. v. Hofmann, *ibid.*, 1887, 20, 2262; W. H. Mills, *T.*, 1922, 121, 455; W. H. Mills and W. T. K. Brauholtz, *ibid.*, 1489.



The virtual tautomerism observed in the case of the *isocyanines* recurs in the *thiocyanines*,<sup>52</sup> for the same methyl diethylthiocyanine iodide (I) is obtained, whether the ethiodides of 5- and 1-methylbenzothiazoles or of 1 : 5-dimethylbenzothiazole and benzothiazole be condensed.



The purple compounds formed simultaneously with the *thiocyanines* correspond with the *carbocyanines*, and are formed in a similar manner by the linking up of two molecules of 1-methylbenzothiazole alkyl halide through a methenyl group derived from the benzothiazole alkyl halide. The synthesis of these *thiocarbocyanines* has been referred to above, although in this case experimental details are not yet available.

*Thioisocyanines* (II) have been synthesised, and resemble the *isocyanines* in their general characters.<sup>53</sup>

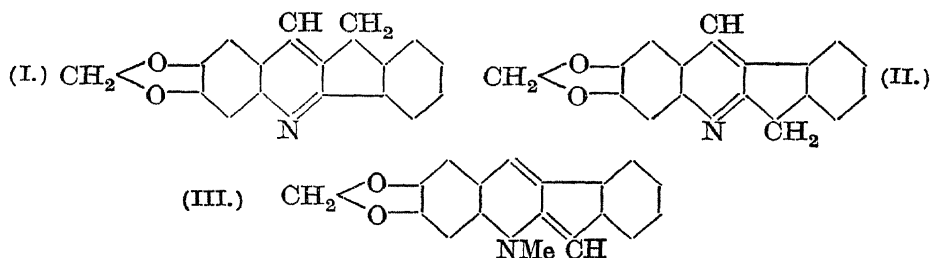
The indenoquinolines (I) and (II) result from the condensation of *o*-aminopiperonal with  $\alpha$ - and  $\beta$ -hydrindones, respectively.<sup>54</sup> The anhydro-base derived from the methosulphate of (II) is purple and therefore is written as (III), the relationship between (II) and (III) being akin to that of the colourless and coloured forms of diquinoxylmethane.<sup>55</sup>

<sup>52</sup> Compare *Ann. Reports*, 1920, 17, 122.

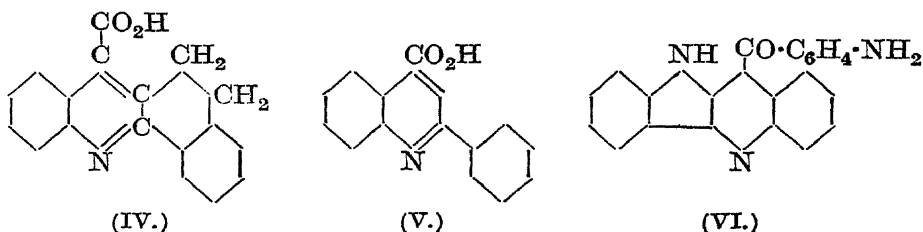
<sup>53</sup> W. T. K. Braunholtz and W. H. Mills, *T.*, 1922, 121, 2004.

<sup>54</sup> J. W. Armit and R. Robinson, *ibid.*, 827.

<sup>55</sup> Compare *Ann. Reports*, 1921, 18, 117.



The condensation of isatin with  $\alpha$ -tetralone (tetrahydro- $\alpha$ -naphthol) in presence of potassium hydroxide is a similar reaction to that just referred to. The product, 3:4-dihydro-1:2-naphthacridine-14-carboxylic acid (IV), is termed tetrophane to recall its similarity in constitution to atophane (V), but the two differ profoundly in their pharmacological action.<sup>56</sup> The new compound resembles strychnine in its action on the spinal cord.



When indigotin is boiled with aniline, preferably in presence of a condensing agent, reaction occurs, probably in the normal manner between the carbonyl and the amino-groups :



The product,<sup>57</sup> which furnishes isatin on oxidation, is rearranged by warm dilute mineral acid to an isomeride, no longer oxidisable to isatin, but which on hydrolysis yields aniline and *o*-amino-benzoyl-5-quindoline (VI).<sup>58</sup>

A number of 9-aminoacridines have been described, and are found to possess bactericidal properties.<sup>59</sup>

The method of separation of *isoquinoline* from coal tar *quinoline* <sup>60</sup> depending on the greater basicity of the former has been improved.<sup>61</sup>

<sup>56</sup> J. v. Braun and P. Wolff, *Ber.*, 1922, **55**, [B], 3675; *A.*, 1923, i, 143.

<sup>57</sup> E. Grandmougin and E. Dessoulavy, *ibid.*, 1909, **42**, 3636, 4401; *A.*, 1909, i, 968; 1910, i, 73.

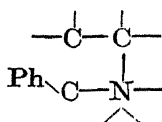
<sup>58</sup> E. Grandmougin, *Compt. rend.*, 1922, **174**, 1175; *A.*, i, 584.

<sup>59</sup> M. L. B., *Brit. Pat.* 176038; *A.*, i, 468.

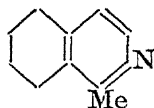
<sup>60</sup> R. Weissgerber, *Ber.*, 1914, **47**, 3175; *A.*, 1915, i, 302.

<sup>61</sup> J. E. G. Harris and (Sir) W. J. Pope, *T.*, 1922, **121**, 1029.

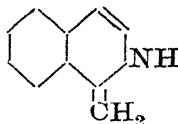
A review of the attempts made to synthesise *isoquinolines* from compounds of the type (I) has led to the conclusion that success is only attained when the compound contains a system of conjugated double bonds, and a hydroxyl or alkyloxy-group in the  $\beta$ -position to the nitrogen atom, or when such a system can be formed in the course of the reaction.<sup>62</sup>



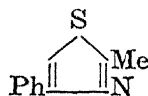
(I)



(II.)



(III.)



(IV.)

It has been shown that 1-, but not 3-, methyl*isoquinoline* contains a reactive methyl group, and that 4-phenyl-2-methyl- (IV), but not 2-phenyl-4-methyl-thiazole is similarly reactive. The difference is attributed either to the direct influence of the double bond between the nitrogen atom and the carbon atom, contiguous to the methyl group, or to the possibility which this confers of the formation of a tautomeride, for example (III).<sup>63</sup>

### *Alkaloids.*

Earlier investigations of ricinine had shown that it responded to the tests for the presence of a glyoxaline ring,<sup>64</sup> contained one methylimino-group,<sup>65</sup> and was broken down by 57 per cent. sulphuric acid into ammonia, carbon dioxide, and a compound,  $C_7H_9O_2N$ . The presence of a pyridine ring in the alkaloid had previously been suspected,<sup>66</sup> and it has now been shown<sup>67</sup> that the product just mentioned is a pyridone, since it is also obtained by spontaneous loss of methyl iodide from 2:4-dimethoxypyridine methiodide (I). Of the two possible formulæ thus indicated, (II) is adopted, because the boiling point of the compound suggests that it is derived from *N*-methyl-2-pyridone rather than from the 4-isomeride, and ricinine is considered to be most probably either (III) or (IV).

<sup>62</sup> P. Staub, *Helv. Chim. Acta*, 1922, **5**, 888; *A.*, 1923, **i**, 140.

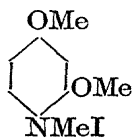
<sup>63</sup> W. H. Mills and J. L. B. Smith, *T.*, 1922, **121**, 2724.

<sup>64</sup> E. Schulze and E. Winterstein, *Z. physiol. Chem.*, 1904, **43**, 211; *A.*, 1905, **ii**, 112; B. Böttcher, *Ber.*, 1918, **51**, 673; *A.*, 1918, **i**, 304.

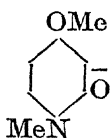
<sup>65</sup> B. Böttcher, *loc. cit.*

<sup>66</sup> L. Maquenne and L. Philippe, *Compt. rend.*, 1904, **138**, 506; **139**, 840; *A.*, 1904, **i**, 339; 1905, **i**, 80; B. Böttcher, *loc. cit.*

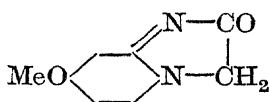
<sup>67</sup> E. Späth and E. Tschelnitz, *Monatsh.*, 1921, **42**, 251; *A.*, **i**, 571.



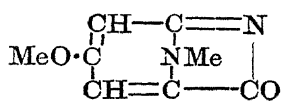
(I.)



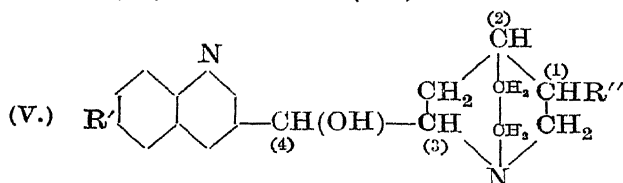
(II.)



(III.)



(IV.)



Of the four asymmetric carbon atoms in the general formula (V) of the cinchona alkaloids, it is already known <sup>68</sup> that the spatial distribution of the groups respectively attached to (1) and (2) is similar in each of the alkaloids, and dextrorotatory in total effect. Also, the stereoisomerism of cinchonine and cinchonidine, or of quinine and quinidine is conditioned by the different distribution round (3). Attention has now been drawn <sup>69</sup> to the fact that of the four possible reduction products of hydrocinchoninone,<sup>70</sup> the most dextrorotatory is dihydrocinchonine, whilst the most lævorotatory is dihydrocinchonidine. If the principle of optical superposition be adopted in a semi-quantitative sense, it follows that in dihydrocinchonine, and hence in cinchonine itself, the effects of (3) and (4) must be both dextrorotatory, whilst in cinchonidine and its dihydro-derivative they are centres of lævorotation. The extension of these conclusions to the other alkaloids is based on a comparison of the rotatory values of the alkaloids, their monochloro-derivatives, and their deoxy-derivatives. This indicates that quinine, dihydroquinine, cinchonidine, dihydrocinchonidine, and ethylhydrocupreine (optochin) are alike in configuration, but differ in this respect from quinidine, hydroquinidine, cinchonine, and hydrocinchonine. A conception of the absolute nature of the spatial distribution of the groups round each of the four carbon atoms in question is still lacking, but appears to be deducible if further investigation should confirm the statement <sup>71</sup> that internal ethers,  $O \begin{smallmatrix} \text{CHMe} \\ \text{CH} \end{smallmatrix} \text{C}_{16}\text{H}_{17}\text{N}_2$ , are obtainable from hydroxydihydrocinchonine but not from hydroxydihydrocinchonidine. For such ether-formation would seem to demand that the  $\cdot\text{CH}_3\cdot\text{CH}(\text{OH})\cdot$

<sup>68</sup> P. Rabe and others, *Annalen*, 1910, **373**, 89; *A.*, 1910, i, 417.

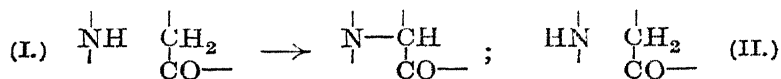
<sup>69</sup> H. King and A. D. Palmer, *T.*, 1922, **121**, 2577.

<sup>70</sup> Compare *Ann. Reports*, 1921, **18**, 140.

<sup>71</sup> Compare *ibid.*, 1920, **17**, 120.

and the  $\cdot\text{CH}(\text{OH})\cdot$  groups, respectively attached to (1) and (3), are on the same side of the piperidine ring structure, but on the opposite side to the methylene groups of the quinuclidine bridge.

It need scarcely be pointed out that the asymmetry of the trivalent nitrogen atom in these alkaloids does not increase the number of isomerides possible, because the spatial distribution of the groups attached to it is not independently variable. This, however, does not apply to the cincho- and quina-toxins, and correspondingly it is found <sup>72</sup> that although the conversion of the toxins prepared from the alkaloids furnishes yields exceeding 80 per cent., these only amount to 50 per cent. when synthetic toxins, presumably composed of a mixture represented by (I) and (II), are employed.



The quinuclidine nucleus would seem to be in some way responsible for the pneumococcal properties of the cinchona alkaloids, since neither dihydroquinatoxin nor the corresponding secondary alcohol is as efficient in this respect as dihydroquinine.<sup>73</sup>

A revision of the results of earlier workers has shown that the quinoline nucleus is attacked when dihydrocinchonine is reduced in amyl-alcoholic solution by sodium. The three products isolated—hexahydrocinchonine, together with epimeric  $\alpha$ - and  $\beta$ -hexahydrodeoxycinchonines—each show the reactions of secondary bases.<sup>74</sup>

On the other hand, it is suggested that the quinuclidine, rather than the quinoline, nucleus is attacked when quinine is converted into an amino-oxide by treatment with hydrogen peroxide. This conclusion is based on the fact that the reaction does not apply to quinoline, but that similar compounds have been obtained from quinidine, dihydrocupreine, and optochin. This argument, however, does not seem very satisfactory, since cinchonine does not react in this manner. Quinine oxide is sufficiently stable to permit of its reduction to dihydroquinine oxide.<sup>75</sup>

The 5-, and, less readily, the 8-amino-groups of 5:8-diamino-6-methoxyquinoline are replaced by hydroxyl when the compound is boiled with hydrochloric acid. 5:8-Diaminodihydroquinoline

<sup>72</sup> P. Rabe, *Ber.*, 1922, 55, [B], 522; *A.*, i, 361; P. Rabe, K. Kindler, and O. Wagner, *ibid.*, 532; *A.*, i, 361.

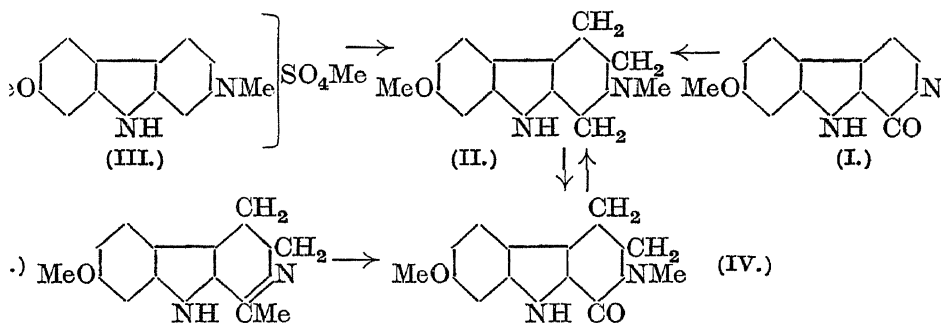
<sup>73</sup> M. Heidelberger and W. A. Jacobs, *J. Amer. Chem. Soc.*, 1922, 44, 1098; *A.*, i, 673.

<sup>74</sup> W. A. Jacobs and M. Heidelberger, *ibid.*, 1079; *A.*, i, 672.

<sup>75</sup> E. Speyer and A. G. Becker, *Ber.*, 1922, 55, [B], 1321; *A.*, i, 674.

reacts still more readily, so that apparently the intermediate hydroxyamino-compound is not isolated. But, on the other hand, 5:8-diaminoquinoline is recovered practically unchanged.<sup>76</sup> This favourable influence of the 6-methoxy-group is also observed in the analogous case of the hydrolysis of benzeneazo-5-aminoquinoline.<sup>77</sup>

The position of the methoxy-group in harmine and harmaline has now been conclusively fixed by the reduction of synthetic methoxyketomethyl-dihydrocarboline (I) (see p. 128) in butyl alcoholic solution by means of sodium to a base, which must be *N*-methyltetrahydronorharmine (II), since it may be similarly obtained from norharmine methosulphate (III) :



Furthermore, synthetic *N*-methyltetrahydronorharmine has been oxidised by potassium permanganate in acetone solution to the neutral substance (IV), originally obtained by similar means from harmaline (V), thus confirming the formulæ of these two compounds. The neutral substance has also been reduced to *N*-methyltetrahydronorharmine.<sup>78</sup>

The oxidation of norharman methosulphate to ketomethyl-dihydrocarboline is evidence that in the free compound addition of methyl sulphate occurs on the pyridine rather than on the pyrrole nitrogen atom, in agreement with an earlier suggestion<sup>79</sup> that the former was the more basic of the two.

In accordance with the formula (I) previously suggested for rutæcarpine, which accompanies evodiamine in *Evodia rutæcarpa*,<sup>80</sup> the former is almost quantitatively converted by treatment with

<sup>76</sup> W. A. Jacobs and M. Heidelberger, *J. Amer. Chem. Soc.*, 1922, **44**, 1073; *A.*, i, 671.

<sup>77</sup> *Ann. Reports*, 1921, **18**, 138.

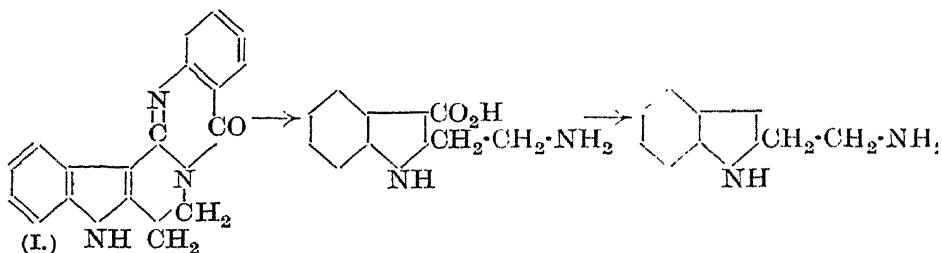
<sup>78</sup> W. O. Kermack, W. H. Perkin, and R. Robinson, *T.*, 1922, **121**, 1872.

<sup>79</sup> W. H. Perkin and R. Robinson, *ibid.*, 1919, **115**, 933.

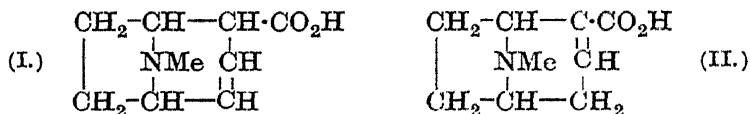
<sup>80</sup> Y. Asahina and S. Mayeda, *J. Pharm. Soc. Japan*, 1916, No. **416**; *A.* 1921, i, 48; compare *Ann. Reports*, 1921, **18**, 142.



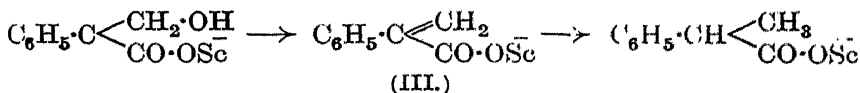
amyl alcohol and potassium hydroxide into 2- $\beta$ -aminoethylindole-3-carboxylic acid, from which 2- $\beta$ -aminoethylindole itself is obtained by means of hydrochloric acid : <sup>81</sup>



A new isomeride of tropine has been isolated from among the basic residues remaining after removal of ecgonine from the products of hydrolysis of the coca alkaloids, but no constitutional formula has been assigned to it.<sup>82</sup> The hydroecgonidine prepared by catalytic reduction of anhydroecgonine consists of two stereoisomerides.<sup>83</sup> It would therefore seem that the older formula<sup>84</sup> for anhydroecgonine (I) must be replaced by (II), and this is supported by the observed exalted molecular refraction of the ethyl ester of anhydroecgonine as compared with that of hydroecgonidine.



The formula attributed to scopoline<sup>85</sup> has been revised on interesting stereochemical grounds. It had previously been a matter for comment that whilst not more than two optically active forms of the alkaloid had been obtained,<sup>86</sup> the products of its hydrolysis were each known to contain asymmetric carbon atoms.<sup>87</sup> Further, when the asymmetry of the tropanyl residue in the alkaloid was destroyed by converting the latter into *aposcopolamine* (III), the latter could not be resolved :



<sup>81</sup> Y. Asahina and A. Fujita, *J. Pharm. Soc Japan*, 1921, 863; *A.*, i, 47.

<sup>82</sup> J. Tröger and K. Schwarzenberg, *Arch. Pharm.*, 1921, 259, 207; *A.*, i, 167.

<sup>83</sup> J. Gadamer and C. John, *ibid.*, 227, 244; *A.*, i, 167, 675.

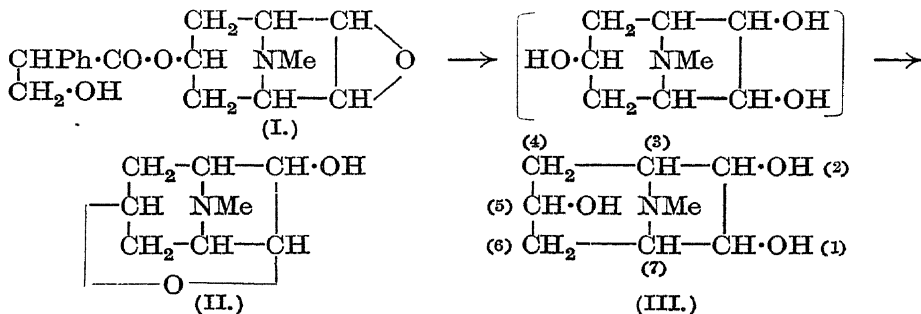
<sup>84</sup> R. Willstätter and W. Müller, *Ber.*, 1898, 31, 2655; *A.*, 1899, i, 178.

<sup>85</sup> Compare *Ann. Reports*, 1920, 17, 127; 1921, 18, 143.

<sup>86</sup> H. King, *T.*, 1919, 115, 476, 974; *Ann. Reports*, 1919, 16, 117.

<sup>87</sup> H. Tutin, *T.*, 1910, 97, 1793.

Again, the *d*-phenylpropionate resulting from the reduction of *aposcopolamine* consisted of only one racemate. When, however, the attempt was made to synthesise the same compound from *scopoline* and *d*-phenylpropionyl bromide, the product was composed of two readily separable racemates. The remarkable conclusion was therefore reached that the alcohol of which *scopolamine* (I) is the ester is probably internally compensated, but suffers a rearrangement, when liberated by hydrolysis, into the asymmetric *scopoline* (II). These relationships are represented as follows : <sup>88</sup>



The formula thus assigned to *scopoline* had been previously suggested <sup>89</sup> to account for its conversion into 1 : 2-dihydroxy-tropane, and for the natural occurrence of *scopolamine* and *tropine* in the same plant. In the formula (III) suggested at the same time for *teloidine*, as a concomitant of the bases just named, the 1- and 5-hydroxyl groups are probably in the *trans*-position, since the formula (II) for *scopoline* shows that *cis*-hydroxyl groups would probably give rise to an oxide ring. A fuller account has also been given of the products obtained by the degradation of *scopoline* by exhaustive methylation.

The structural relationship so frequently observed between alkaloids which occur together is also well illustrated by the formulæ assigned to five of the seven known cactus alkaloids. *Anhaline* (I) has been identified with *hordenine*,<sup>90</sup> whilst *mezcaline* (II) is known to be  $\beta$ -3 : 4 : 5-trimethoxyphenylethylamine.<sup>91</sup> It has now been shown <sup>92</sup> that *N*-acetylmezcaline may be converted by the usual means into 6 : 7 : 8-trimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, from which by reduction the corresponding

<sup>88</sup> K. Hess and O. Wahl, *Ber.*, 1922, 55, [B], 1979; *A.*, i, 854.

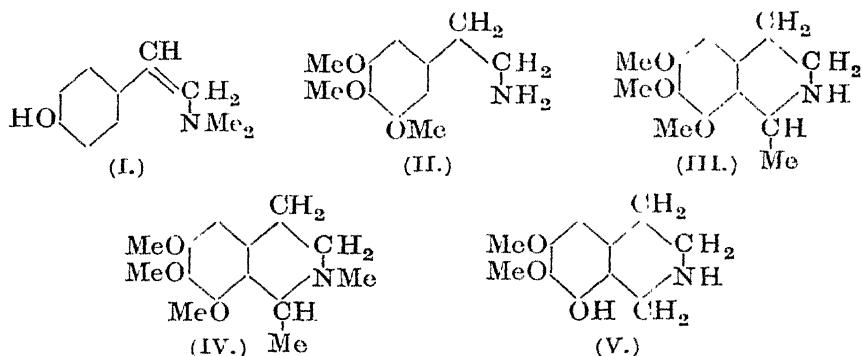
<sup>89</sup> H. King, *loc. cit.*, p. 487.

<sup>90</sup> E. Späth, *Monatsh.*, 1919, 40, 129; 1921, 42, 263; *A.*, 1919, i, 548; 1922, i, 567.

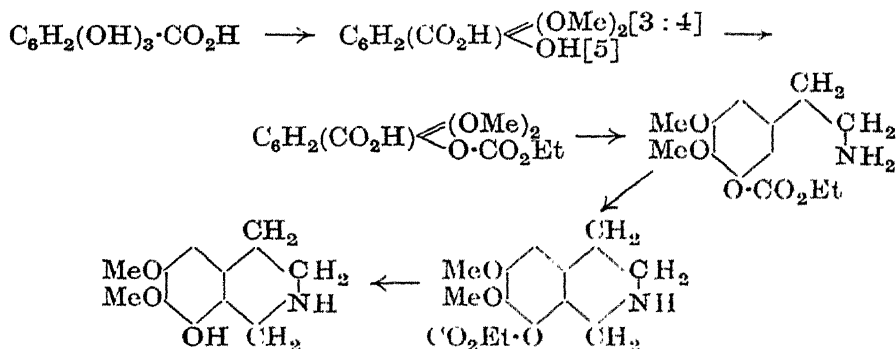
<sup>91</sup> *Idem*, *ibid.*, 1919, 40, 129; *A.*, 1919, i, 548; compare *Ann. Reports*, 1919, 16, 123.

<sup>92</sup> *Idem*, *ibid.*, 1921, 42, 97; *A.*, i, 163.

tetrahydroisoquinoline is obtained. This, and its *N*-methyl derivative, are



respectively identical with the *O*-methyl derivatives of anhalonidine (III) and pellotine (IV). It therefore only remains to determine which of the three methoxy-groups of the synthetic compounds corresponds with the phenolic hydroxyl in the two alkaloids. The probable mode of attacking this problem is indicated by that successfully adopted in the case of anhalamine (V), and indicated in the following scheme representing the synthesis of this base from gallic acid :<sup>93</sup>



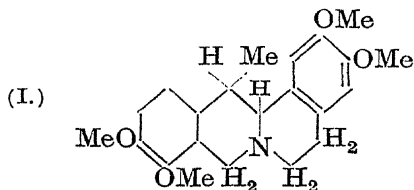
Again, the bases which accompany palmatine in the calumba root, and are separated from it by successively extracting the mixture of the iodides of the bases with potassium carbonate and with potassium hydroxide, are now shown to furnish on methylation products, not only identical with each other, but also with palmatine. The identity also extends to the tetrahydro-bases and therefore it follows that the calumba root contains besides palmatine, phenolic bases having one or more free hydroxyl groups

<sup>93</sup> E. Späth and H. Röder, *Monatsh.*, 1922, 43, 93; *A.*, i, 852.

in place of methoxyl groups in palmatine, or else phenolic oxygen combined with complexes easily removable by hydrolysis. It should be noted, however, that the homogeneity of the above two basic extracts, columbamine and iatrorrhicine, is not quite certain.<sup>94</sup>

The formula previously assigned to laudanine<sup>95</sup> has been confirmed by synthesis.<sup>96</sup> This follows the course now so familiar as to be almost conventional in such cases, and furnishes another illustration (compare the synthesis of anhalamine, above) of the device of masking a phenolic hydroxyl group throughout such a synthesis by its conversion at the outset into an ethylcarbonato-group, from which it can be regenerated at the conclusion.

The need for a revision of the formula of corydaline has been admitted, and (I) is now suggested, since dehydrocorydaline, derived by removal of four hydrogen atoms through the agency of mercuric acetate, is found to undergo the Cannizzaro reaction with sodium hydroxide.<sup>97</sup>



Passing reference has already been made to an investigation of isochondodendrine, in which considerable progress has been made towards the determination of its constitution. But it would seem advisable to defer a fuller account of this until one or two outstanding points have been cleared up by further investigation.

Several papers have appeared on the chemistry of the morphine alkaloids and of strychnine, but these are not of a character which may usefully be dealt with here.

J. KENNER.

<sup>94</sup> E. Späth and K. Böhm, *Ber.*, 1922, **55**, [B], 2985; *A.*, i, 1174.

<sup>95</sup> Compare *Ann. Reports*, 1921, **17**, 144.

<sup>96</sup> E. Späth and N. Lang, *Monatsh.*, 1921, **42**, 273; *A.*, i, 568.

<sup>97</sup> J. Gadamer and F. von Bruckhausen, *Arch. Pharm.*, 1922, **259**, 245; *A.*, i, 675.

## ANALYTICAL CHEMISTRY\*.

THE number of analytical papers now being published has fully reached the standard of the years before the war, and therefore the prefatory remarks to last year's Report are still more applicable to the present Report.

### *Physical Methods.*

The useful process of separating the constituents of minerals by treatment with liquids of different density has been extended by the introduction of three colourless liquids, namely, barium bromomercurate solution, saturated aqueous thallium formate solution, and a mixture of aqueous solutions of thallium formate and malonate. By using these at different temperatures a range of density from 3.1 to more than 5 is obtained.<sup>1</sup>

There have been several new applications of spectroscopy to analytical work. For example, it has been shown that the spectroscope affords the most accurate means of distinguishing between caesium and rubidium;<sup>2</sup> also, that germanium may be easily identified by its arc spectrum, which shows a characteristic line in the blue region.<sup>3</sup>

In a further development of a research on spectrophotometry<sup>4</sup> it has been found that the method, when used in conjunction with data previously recorded, will enable the proportion of enol in keto-enol mixtures to be estimated with a fair degree of accuracy, provided it is possible to ascertain the optical constants of the respective pure constituents.<sup>5</sup>

By making mixtures of pure argon with pure xenon and with pure krypton, and determining the pressure at which the spectrophotometric intensity of selected lines in the spectra of the respective mixtures becomes equal to that of corresponding selected lines in the argon spectrum, it has been found possible to calculate the proportions of xenon and krypton in the two mixtures.<sup>6</sup>

<sup>1</sup> E. Clerici, *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 116; *A.*, ii, 578.

<sup>2</sup> J. Missenden, *Chem. News*, 1922, **124**, 362; *A.*, ii, 658.

<sup>3</sup> J. Papish, *ibid.*, 3; *A.*, ii, 163.

<sup>4</sup> K. von Auwers and H. Jacobsen, *Annalen*, 1918, **415**, 169; *A.*, 1918, ii, 381.

<sup>5</sup> *Idem*, *ibid.*, 1922, **426**, 161; *A.*, ii, 168.

<sup>6</sup> C. Moureu and A. Lepape, *Compt. rend.*, 1922, **174**, 908; *A.*, ii, 394.

The difference in the colour reactions of methylfurfuraldehyde and hydroxymethylfurfuraldehyde when converted into phloroglucides may be sharply distinguished by the use of the ultra-violet spectroscope.<sup>7</sup>

Mention may also be made of a new method of colour measurement based upon spectrophotometric measurements.<sup>8</sup>

The more recent work on nephelometry has included a study of the cause of the deviations from the proportionality between the amount of diffracted light and the concentration of coloured sols and turbidities. It is due to the selective absorption of light by the coloured particles, and may be prevented by the use of suitable light filters placed between the source of light and the nephelometer.<sup>9</sup>

A new type of nephelometer has also been devised in which the two fields are made concentric. By using two Nicol prisms, by which the light can be registered and regulated, in place of one of the tube systems in this instrument, a permanent standard may be established.<sup>10</sup>

An optical method of estimating the colloidal portion of tungsten powder has been based on the absorption of light from a quartz-mercury lamp by the solution from which the powder has sedimented, and the measurement of the absorption by the deflection of a galvanometer when the light passing through the solution is received on a potassium photo-electric cell.<sup>11</sup>

A new principle of estimating unweighable quantities of metals such as lead or bismuth consists in the use of the radioactive isotopes of the metals as indicators. Since the active and inactive isotopes, when once mixed, cannot be separated by chemical methods, the detection of the former by means of the electroscope is also an indication of the presence of the latter.<sup>12</sup>

Another application of the electroscopic method of analysis has been its use in the estimation of thorium in monazite sand by means of the emanation. The percentage of thorium-X is calculated from the electroscope readings by means of the formula

$$X = AT_s(T_b - T_u)/T_s(T_b - T_s),$$

where  $A$  represents the proportion of thorium in a standard sample,  $T_s$  the time of discharge of the electroscope by this standard

<sup>7</sup> J. Tadokoro, *J. Coll. Agric. Hokkaido Imp. Univ.*, 1921, **10**, 52; *A.*, ii, 236.

<sup>8</sup> H. E. Ives, *J. Opt. Soc. Amer.*, 1921, **5**, 469; *A.*, ii, 221.

<sup>9</sup> H. Bechhold and F. Hebler, *Kolloid Z.*, 1922, **31**, 7; *A.*, ii, 652.

<sup>10</sup> A. A. Weinberg, *Biochem. Z.*, 1921, **125**, 292; *A.*, ii, 309.

<sup>11</sup> A. Lottermoser, *Kolloid Z.*, 1922, **30**, 53; *A.*, ii, 230.

<sup>12</sup> F. Paneth, *Z. angew. Chem.*, 1922, **35**, 549; *A.*, ii, 785.

sample,  $T_b$  the time of discharge by a blank sample free from thorium, and  $T_u$  by the sample under examination.<sup>13</sup>

A new thermometric method of titrating acids has been devised, the solution being mechanically stirred in a vacuum tube, while alkali solution is added at regular intervals in amounts causing the temperature to increase by not more than  $0.02^\circ$ . When the temperature readings are plotted as ordinates and the number of c.c. of alkali as abscissæ, a decided change in the direction of the curve indicates the end-point. The method not only gives results identical with those given by electrometric methods, but also indicates other points at which changes in the nature of the reaction take place.<sup>14</sup>

### *Gas Analysis.*

The most suitable concentration of pyrogallol solution for absorption of oxygen in gas analysis has been ascertained by tabulating the absorptive capacities of solutions of all concentrations in a Gibbs triangular diagram for the system pyrogallol, potassium hydroxide, and water. By this means it has been found that the best results are obtained by the use of a solution of 20 parts of pyrogallol and 20 parts of potassium hydroxide in 60 parts of water.<sup>15</sup>

It has also been shown that in using acid cuprous chloride solution as an absorbent for carbon monoxide the rate of absorption and the stability of the reagent are increased by the addition of stannous chloride.<sup>16</sup>

For the accurate estimation of hydrogen in the presence of gaseous paraffins advantage has been taken of its reducing action on palladous chloride, the separated palladium being collected, dried, and weighed, and calculated into the equivalent amount of hydrogen.<sup>17</sup>

Various absorbents have been tried for the estimation of hydrogen phosphide. The gas is completely absorbed by iodic acid solution within thirty minutes, and by distilling the liberated iodine into potassium iodide solution and titrating the liquid it is possible to estimate the phosphine. Or the phosphoric acid in the flask may be estimated as magnesium pyrophosphate. Another method is to absorb the hydrogen phosphide in standard silver nitrate, mercuric chloride, or gold chloride solution, and to estimate the phos-

<sup>13</sup> H. H. Helmick, *J. Amer. Chem. Soc.*, 1921, **43**, 2003; *A.*, ii, 164.

<sup>14</sup> P. Dutoit and E. Grobet, *J. Chim. physique*, 1922, **19**, 324; *A.*, ii, 578.

<sup>15</sup> F. Hoffmann, *Z. angew. Chem.*, 1922, **35**, 451; *A.*, ii, 582.

<sup>16</sup> A. Kropf, *ibid.*, 451; *A.*, ii, 657.

<sup>17</sup> J. A. Muller and A. Foix, *Bull. Soc. chim.*, 1922, [iv], **33**, 713; *A.*, ii, 655.

phoric acid in the filtrate from the precipitated silver, etc.<sup>18</sup> A special form of absorption apparatus for this process has been devised.<sup>19</sup>

The absorption of carbon dioxide formed in the estimation of minute quantities of methane may be rapidly effected in one vessel by adding gelatin solution to the baryta absorbent, the resulting scum prolonging the contact of the gases with the reagent.<sup>20</sup>

Further particulars have been published of the method of estimating benzene by absorption with charcoal.<sup>21</sup> A correction for the benzene retained by the charcoal is found by means of a control test.<sup>22</sup>

An accurate thermometric method of estimating minute quantities (0.001 to 1 per cent.) of oxygen in hydrogen consists in passing the gas through a platinised catalyst at 305°, and measuring the rise in temperature, caused by the combustion of the hydrogen, by means of a thermo-element connected with a galvanometer.<sup>23</sup>

Another method of estimating traces of oxygen, which is particularly suitable for biochemical work, is to convert the oxygen, by means of nitric oxide and sodium hydroxide, into sodium nitrite, which is then estimated colorimetrically by means of sulphanilic acid and  $\alpha$ -naphthylamine.<sup>24</sup>

It has been found that when air is used as the source of oxygen in slow combustion and explosion methods of gas analysis no appreciable error results if the time of burning does not exceed three minutes and the platinum wire is not heated too strongly. Otherwise, an error of as much as 2 per cent. may be caused by the formation of oxides of nitrogen.<sup>25</sup>

When estimating nitrogen peroxide and nitric oxide in gas mixtures by absorption with alkali solutions it is necessary to take into consideration the fact that if a mist has previously developed, owing to chilling of the gas, some of the nitrogen peroxide will have been converted into nitric acid and nitric oxide, and that these constituents must be absorbed and included in the calculations.<sup>26</sup>

Traces of oxides of nitrogen in air may be accurately estimated

<sup>18</sup> L. Moser and A. Brukl, *Z. anorg. Chem.*, 1921, **121**, 73; *A.*, ii, 393.

<sup>19</sup> L. Moser, *ibid.*, 1922, **121**, 313; *A.*, ii, 519.

<sup>20</sup> E. Murmann, *Oesterr. Chem. Ztg.*, 1922, **25**, 90; *A.*, ii, 591.

<sup>21</sup> Compare *Ann. Reports*, 1921, **18**, 149.

<sup>22</sup> E. Berl, *Z. angew. Chem.*, 1922, **35**, 332; *A.*, ii, 591.

<sup>23</sup> A. T. Larson and E. C. White, *J. Amer. Chem. Soc.*, 1922, **44**, 20; *A.*, ii, 311.

<sup>24</sup> H. M. Sheaff, *J. Biol. Chem.*, 1922, **52**, 35; *A.*, ii, 582.

<sup>25</sup> G. W. Jones and W. L. Parker, *J. Ind. Eng. Chem.*, 1921, **13**, 1154; *A.*, ii, 223.

<sup>26</sup> C. L. Burdick, *ibid.*, 1922, **14**, 308; *A.*, ii, 583.



by oxidising them with sodium hydroxide solution and hydrogen peroxide, and estimating the resulting nitrate colorimetrically by the phenoldisulphonic acid method.<sup>27</sup>

Oxidation with hydrogen peroxide (perhydrol) in alkali solution is also the basis of a method of estimating sulphur compounds of all kinds in coal gas,<sup>28</sup> and hydrogen peroxide is recommended as an absorbent for sulphurous acid in air.<sup>29</sup>

In connexion with this branch of analysis, mention may also be made of a process of estimating gases in metals. A special form of apparatus connected with a Toeppler pump is used, and the gases collected from a weighed quantity of the metal are examined spectroscopically and then analysed by the usual methods.<sup>30</sup>

### *Agricultural Analysis.*

Considerable attention has been given to the standardisation of the methods for the mechanical analysis of soils, and a rapid method has been devised in which measured amounts of a suspension of the soil in a 0.025 per cent. sodium carbonate solution are withdrawn at measured intervals and a relationship (expressed graphically) is established between the percentage of soil and the rate of sedimentation.<sup>31</sup> In order to render humus soils suitable for mechanical analysis, it is necessary to destroy the organic matter. This may be conveniently done by heating the soil with hydrogen peroxide.<sup>32</sup>

For the estimation of humus in soils the carbon dioxide present as carbonate is first removed, and the soil then oxidised with sulphuric acid and potassium dichromate, the gases from the oxidation are conducted through copper oxide and lead chromate, and the carbon dioxide is absorbed and weighed.<sup>33</sup>

It has been shown that the use of a carbon factor for calculating the amount of organic matter in a soil is of questionable value, and that, in any case, results closer to the truth will be obtained by taking the relationship of 50 to 52 per cent. of carbon to represent 100 parts of soil, instead of 58 per cent. as at present.<sup>34</sup>

¶ The amount of moisture in soil may be calculated from the

<sup>27</sup> V. C. Allison, W. L. Parker, and G. W. Jones, *U.S. Bureau of Mines, Techn. Paper*, 249; *A.*, ii, 313.

<sup>28</sup> A. Klemmer, *Chem. Ztg.*, 1922, 46, 79; *A.*, ii, 224.

<sup>29</sup> G. Lambert, *Z. anal. Chem.*, 1922, 61, 20; *A.*, ii, 390.

<sup>30</sup> H. L. Simons, *Chem. Met. Eng.*, 1922, 27, 248; *A.*, ii, 719.

<sup>31</sup> G. W. Robinson, *J. Agric. Sci.*, 1922, 12, 306; *A.*, ii, 888.

<sup>32</sup> *Idem*, *ibid.*, 287; *A.*, ii, 888.

<sup>33</sup> A. Gehring, *Z. anal. Chem.*, 1922, 61, 293.

<sup>34</sup> J. W. Read and R. H. Ridgell, *Soil Sci.*, 1922, 13, 1; *A.*, ii, 540.

measurement, under specified conditions, of the resistance between two carbon electrodes placed in the soil.<sup>35</sup>

A method of estimating the acidity or basicity of a soil, and also the amount of soluble iron or aluminium salts, depends on extracting the soil with alcoholic potassium thiocyanate solution, and titrating the extract with standard alcoholic alkali or acid. The use of logwood enables a colorimetric estimation of aluminium to be made.<sup>36</sup>

Further evidence has been adduced of the untrustworthiness of citric solubility as a criterion of the agricultural value of mineral phosphates, the amounts of extract obtainable varying with the conditions.<sup>37</sup> A modified method of estimating phosphoric acid has been devised, in which the precipitation with ammonium molybdate is effected in the cold, and the precipitate ultimately dried at 120° and weighed. Less variation in composition thus results than in the case of precipitates obtained in the usual way.<sup>38</sup>

In a combined method of estimating total nitrogen, nitric nitrogen, and nitrous nitrogen in fertilisers, the total nitrogen is first estimated after reduction with ferrum redactum; the nitrites are removed by distillation as methyl esters, the residual nitrates reduced as before, and the ammonia distilled.<sup>39</sup> The digestion with acid in the Kjeldahl flask may be greatly accelerated by the addition of mercurous iodide, which is much more effective than mercury or other mercury salts.<sup>40</sup>

A simple method of overcoming the difficulty of estimating guanidine when guanylcarbamide is present as an impurity is to precipitate the guanidine as picrate from a solution of sodium hydroxide, leaving the guanylcarbamide picrate in solution.<sup>41</sup> The conditions under which triketohydrindene (ninhydrin) can be used as a quantitative colorimetric reagent for the estimation of amino-acid nitrogen have been worked out, and it has been shown that histidine is the only amino-acid which gives a coloration differing slightly from the standard.<sup>42</sup>

### *Organic Analysis.*

*Qualitative.*—A general reaction enabling fatty acids of the acetic series to be detected has been found in the formation of their

<sup>35</sup> T. Deighton, *J. Agric. Sci.*, 1922, **12**, 207.

<sup>36</sup> R. H. Carr, *J. Ind. Eng. Chem.*, 1921, **13**, 931; *A.*, ii, 172.

<sup>37</sup> J. F. Tocher, *J. Agric. Sci.*, 1922, **12**, 125; *A.*, ii, 525.

<sup>38</sup> A. W. Clark and R. F. Keeler, *J. Assoc. Off. Agric. Chem.*, 1921, **5**, 103; *A.*, ii, 84.

<sup>39</sup> F. Mach and F. Sindlinger, *Z. angew. Chem.*, 1922, **35**, 473; *A.*, ii, 783.

<sup>40</sup> M. and I. Sborowsky, *Ann. Chim. anal.*, 1922, **4**, 266; *A.*, ii, 783.

<sup>41</sup> A. H. Dodd, *J. Soc. Chem. Ind.*, 1922, **41**, 445T; *A.*, ii, 536.

<sup>42</sup> H. Riffart, *Biochem. Z.*, 1922, **131**, 78; *A.*, ii, 718.

double sodium uranyl salts, which form characteristic micro-crystalline precipitates.<sup>43</sup>

Other microchemical group reagents are iodic acid, which yields distinctive precipitates with alkaloids and organic bases,<sup>44</sup> and picric acid, which, under standard conditions, forms crystalline picrates of different form with vegetable alkaloids.<sup>45</sup> Veronal and other hypnotics derived from barbituric acid form crystalline dixanthyl derivatives of various melting points, whereas other hypnotics do not react in this way with xanthhydrol.<sup>46</sup>

A stable modification of Schiff's reagent for aldehydes has been prepared from rosaniline hydrochloride and sodium hyposulphite. It can be heated to accelerate the reaction with aldehydes.<sup>47</sup>

The phenol test for formaldehyde is not trustworthy when applied to the distillate from oxidised spirits and tinctures. A solution of guaiacol or apomorphine in concentrated sulphuric acid gives more definite results. The former reagent gives a dark red coloration with formaldehyde, and the latter a distinctive precipitate.<sup>48</sup>

The well-known colour reaction of liver oils with sulphuric acid has been shown to stand in some relationship to the vitamin content of the oil, and the test has been applied quantitatively by a method of dilution until the colour is no longer produced.<sup>49</sup> Liquid paraffin (B.P.) is a suitable diluting agent for this purpose.<sup>50</sup>

A new test for carbohydrates has been based on the formation of acetal, identified by its blue fluorescence and by the formation of 3-hydroxy-2-methylquinoline. The acetal reaction is given by all the common sugars and by dextrin, but not by glycerol, starch, or glycogen.<sup>51</sup>

When sucrose is boiled with a saturated solution of ammonium nickel sulphate and a few drops of sulphuric or hydrochloric acid, it gives a distinctive red coloration.<sup>52</sup> Another test for sucrose in the presence of dextrose has been based upon the fact that the

<sup>43</sup> J. Barlot and (Mlle) M. T. Brenet, *Compt. rend.*, 1922, 174, 114; *A.*, ii, 167.

<sup>44</sup> L. Rosenthaler, *Schweitz Apoth. Ztg.*, 1921, 59, 477; *A.*, ii, 327.

<sup>45</sup> B. E. Nelson and H. A. Leonard, *J. Amer. Chem. Soc.*, 1922, 44, 369; *A.*, ii, 327.

<sup>46</sup> R. Fabre, *J. Pharm. Chim.*, 1922, [vi], 26, 241; *A.*, ii, 795.

<sup>47</sup> E. Wertheim, *J. Amer. Chem. Soc.*, 1922, 44, 1834; *A.*, ii, 793.

<sup>48</sup> B. Peyl, G. Reif, and A. Hanner, *Chem. Ztg.*, 1921, 45, 1220; *A.*, ii, 94.

<sup>49</sup> J. C. Drummond and A. F. Watson, *Analyst*, 1922, 47, 341; *A.*, ii, 665.

<sup>50</sup> H. D. Richmond and E. H. England, *ibid.*, 431; *A.*, ii, 792.

<sup>51</sup> O. Baudisch and H. J. Deuel, *J. Amer. Chem. Soc.*, 1922, 44, 1585; *A.*, ii, 664.

<sup>52</sup> F. Krys, *Oesterr. Chem. Ztg.*, 1921, 24, 141; *A.*, ii, 233.

former is soluble and the latter insoluble, in hot ethyl acetate.<sup>53</sup> Lævulose may be detected in the presence of aldoses by the fact that, after treatment with iodine solution and then with sodium hydroxide, it gives a red coloration with Fehling's solution within four minutes, whilst dextrose does not react until after five minutes' heating.<sup>54</sup>

An acidified solution of benzidine hydrochloride gives an orange coloration with ligneous tissue, and since starch can be stained with iodine in the same section, the reagent will be of value in biochemical work.<sup>55</sup>

In this connexion mention should also be made of a qualitative test for tannin based on its fixation on gold-beater's skin, which can then be stained with dilute ferric chloride solution.<sup>56</sup>

An acidified solution of *p*-nitroaniline hydrochloride, decolorised with sodium nitrite, has been found to be a sensitive reagent for phenols, which, when treated with it and with excess of sodium hydroxide, give colorations ranging from salmon pink to ruby-red, according to the quantity of phenol present. The test will detect 1 part of ordinary phenol in 1,000,000.<sup>57</sup>

A method of distinguishing between phenacetin and acetanilide depends on the difference in the colorations given by the two substances when hydrolysed with sulphuric acid and oxidised with potassium dichromate.<sup>58</sup>

Traces of pyridine may be detected by the formation of a red, crystalline compound, 1-anilinodihydropyridinium phenyl bromide, on treatment with aniline in the presence of water and cyanogen bromide.<sup>59</sup> The test is capable of detecting 1 part of pyridine in 350,000 parts of water.<sup>60</sup>

A new method of estimating the pyrimidine, thymine, has been based on its oxidation into carbamide, acetylcarbinol, and pyruvic acid, and identification of the pyruvic acid by converting it into indigotin.<sup>61</sup>

*Quantitative.*—There have been several contributions to the method of ultimate analysis. Thus it has been shown that in the wet combustion of organic compounds good results are obtained

<sup>53</sup> L. A. Congdon and C. R. Steward, *J. Ind. Eng. Chem.*, 1921, **13**, 1143; *A.*, ii, 233.

<sup>54</sup> I. M. Kolthoff, *Chem. Weekblad*, 1922, **19**, 1; *A.*, ii, 166.

<sup>55</sup> C. van Zijp, *Pharm. Weekblad*, 1921, **58**, 1539; *A.*, ii, 94.

<sup>56</sup> E. Atkinson and E. O. Hazleton, *Biochem. J.*, 1922, **16**, 516; *A.*, ii, 793.

<sup>57</sup> J. Moir, *J. S. African Chem. Inst.*, 1922, **5**, 8; *A.*, ii, 321.

<sup>58</sup> L. Elkkert, *Pharm. Zentr.-h.*, 1921, **62**, 735; *A.*, ii, 169.

<sup>59</sup> A. Goris and A. Larssonneau, *Bull. Soc. Pharmacol.*, 1921, **28**, 497; *A.*, ii, 795.

<sup>60</sup> F. Lehnor, *Chem. Ztg.*, 1922, **46**, 877; *A.*, ii, 795.

<sup>61</sup> A. Baudisch and T. B. Johnson, *Ber.*, 1922, **55**, [B], 18; *A.*, ii, 238.

by the use of a mixture of silver chromate and sulphuric acid as the oxidising agent.<sup>62</sup> The method has its drawbacks, however, for it is only applicable to certain types of compounds, such as sugars not containing a methyl group attached directly to a carbon group.<sup>63</sup> The oxidising action of the sulpho-chromic mixture may be increased by the addition of chromic oxide, and the scope of the method thus extended.<sup>64</sup>

A volumetric method of estimating carbon and hydrogen is to pass the gaseous products of the combustion first over a substance, such as chloronaphthyloxychlorophosphine, which yields hydrogen chloride on hydrolysis, and then into standard baryta solution, which is afterwards titrated with standard hydrochloric acid. The carbon dioxide is then removed from the baryta solution after addition of excess of acid, and the residual solution again titrated, this time with standard baryta solution.<sup>65</sup>

For the direct estimation of oxygen the organic substance is heated in a current of hydrogen, and the water formed in the hydrogenation collected and weighed. The method is unsuitable for nitrogen compounds, which yield ammonia on hydrogenation.<sup>66</sup>

A rapid method of estimating chlorine consists in absorbing the products of combustion in water and titrating the absorbed chloride with a mercuric salt, with the use of sodium nitroprusside as indicator.<sup>67</sup>

The low results obtained by the Knecht-Hibbert method of reduction in the estimation of the nitro-groups in certain aromatic compounds has been shown to be due to chlorination reactions. The difficulty can be overcome by using titanous sulphate instead of titanous chloride for the reduction.<sup>68</sup>

Nessler's reagent may be used, not only for the characterisation of aldehydes and ketones, but also for the estimation of certain aldehydes, the iodine liberated in the reaction being titrated with thiosulphate.<sup>69</sup> Another method which is applicable to various aldehydes and ketones is based on the hydroxylamine method<sup>70</sup> of estimating citral.<sup>71</sup>

<sup>62</sup> L. J. Simon, *Compt. rend.*, 1922, 174, 1706; *A.*, ii, 593.

<sup>63</sup> L. J. Simon and A. J. A. Guillaumin, *ibid.*, 175, 525; *A.*, ii, 867.

<sup>64</sup> L. J. Simon, *ibid.*, 768; *A.*, ii, 868.

<sup>65</sup> J. Lindner, *Ber.*, 1922, 55, [B], 2025; *A.*, ii, 657.

<sup>66</sup> R. ter Meulen, *Rec. trav. chim.*, 1922, 41, 509; *A.*, ii, 717.

<sup>67</sup> E. Votocěk, *Chem. Listy*, 1922, 16, 248; *A.*, ii, 863.

<sup>68</sup> T. Callan and J. A. R. Henderson, *J. Soc. Chem. Ind.*, 1922, 41, 157r; *A.*, ii, 524.

<sup>69</sup> J. Bougault and R. Gros, *J. Pharm. Chim.*, 1922, 26, 5; *A.*, ii, 666.

<sup>70</sup> A. H. Bennett, *Analyst*, 1909, 34, 12; *A.*, 1909, ii, 192.

<sup>71</sup> A. H. Bennett and F. K. Donovan, *ibid.*, 1922, 47, 146; *A.*, ii, 535.

A direct method of estimating acetaldehyde is to treat the solution with excess of an alkaline ammoniacal silver solution and to titrate the reduced silver with ammonium thiocyanate solution.<sup>72</sup> A rapid colorimetric method has also been based on the fact that acetaldehyde gives a yellow coloration with benzidine hydrochloride.<sup>73</sup> An analogous method for estimating furfuraldehyde depends on the coloration which it gives with orcinol.<sup>74</sup>

The conditions affecting the quantitative estimation of reducing sugars by means of Fehling's solution have been studied and means for avoiding some of the errors in the current methods have been devised.<sup>75</sup> It has been found that sucrose is slowly hydrolysed by Fehling's solution to an extent depending on the conditions, and that a blank estimation should therefore be made.<sup>76</sup>

A new method of estimating sucrose consists in heating the sugar with lime and water at 60—80°, and polarising the solution, in which sugars other than sucrose will have been destroyed.<sup>77</sup> The use of invertase for the estimation of sucrose has also been recommended.<sup>78</sup> Numerous errors are involved in the estimation of sugar in urine by fermentation with yeast. They may be reduced to some extent by sterilisation and precipitation of carbonates in the urine with calcium chloride.<sup>79</sup>

The estimation of anthraquinone by the method of Lewis<sup>80</sup> involves certain filtration difficulties; these may be avoided by using a volumetric method of estimation.<sup>81</sup>

A gravimetric method of estimating phenanthrene is based on its oxidation by means of iodic acid to phenanthraquinone, which is then precipitated as toluphenanthrazine by means of 3 : 4-tolylene-diamine.<sup>82</sup>

A critical survey of the various methods of estimating alkaloids has been made and the conclusion drawn that, of the gravimetric methods, only precipitation with picric acid, phosphotungstic or silicotungstic acid or with picrolonic acid gives serviceable results, whilst of the volumetric methods titration with standard acid is

<sup>72</sup> W. Stepp and R. Fricke, *Z. physiol. Chem.*, 1921, **116**, 293; *A.*, ii, 236.

<sup>73</sup> N. K. Smitt, *Bull. Bur. Bio-Techn.*, 1922, No. 5, 117; *A.*, ii, 402.

<sup>74</sup> P. Fleury and G. Poirot, *J. Pharm. Chim.*, 1922, [vii], **26**, 87; *A.*, ii, 666.

<sup>75</sup> F. A. Quisumbing and A. W. Thomas, *J. Amer. Chem. Soc.*, 1921, **43**, 1503; *A.*, ii, 92.

<sup>76</sup> E. Canals, *Bull. Soc. chim.*, 1922, [iv], **31**, 583; *A.*, ii, 592.

<sup>77</sup> A. Behre and A. Düring, *Z. Unters. Nahr. Genussm.*, 1922, **44**, 65; *A.*, ii, 790.

<sup>78</sup> T. S. Harding, *Sugar*, 1921, **23**, 546; *A.*, ii, 167.

<sup>79</sup> C. Lange, *Berlin Klin. Woch.*, 1921, **58**, 957; *A.*, ii, 93.

<sup>80</sup> H. F. Lewis, *J. Ind. Eng. Chem.*, 1918, **10**, 425; *A.*, 1918, ii, 338.

<sup>81</sup> O. A. Nelson and C. E. Senseman, *ibid.*, 1922, **14**, 956; *A.*, ii, 882.

<sup>82</sup> A. G. Williams, *J. Amer. Chem. Soc.*, 1921, **43**, 1911; *A.*, ii, 90.

the most trustworthy.<sup>83</sup> Caffeine gives an insoluble precipitate with silicotungstic acid and may be added to the list of alkaloids which can be estimated by means of that reagent.<sup>81</sup>

New methods of estimating morphine, codeine, and narcotine in Indian opium have been described,<sup>85</sup> and a method of estimating meconic acid in opium, based on its separation as calcium meconate.<sup>86</sup>

Considerable attention has been given to the estimation of uric acid, and various modifications and colorimetric methods have been suggested, including one in which an arsenotungstic acid reagent is used<sup>87</sup> in place of the original phosphotungstic acid reagent of Folin and Denis.<sup>88</sup>

### *Inorganic Analysis.*

*Qualitative.*—A scheme for separating metals by the use of sodium sulphide instead of hydrogen sulphide has been devised, the reagent being added to the hydrochloric acid solution, which has previously been neutralised with sodium carbonate and boiled with dilute sodium hydroxide solution. The resulting precipitate may contain the sulphides, hydroxides, and carbonates of one group of metals, and the filtrate the sulphides of another group.<sup>89</sup> In another scheme of separation no sulphur compounds are used, but nascent hydrogen is produced, as in the Marsh test, in the hydrochloric acid solution. A group, which may contain silver, mercury, lead, bismuth, copper, cadmium, platinum, gold, tin, antimony, and arsenic, is thus precipitated.<sup>90</sup>

A new reagent for microchemical analysis has been found in caesium chloride, which forms characteristic double chlorides with a large number of metals.<sup>91</sup>

Another sensitive reagent, giving distinctive colorations with certain metals, is a mixture of resorcinol solution and ammonia.<sup>92</sup>

In addition to these group reagents, several useful tests for individual anions have been published. For example, the Kastle-Meyer reagent (an alkaline solution of phenolphthalein decolorised

<sup>83</sup> P. Herzig, *Arch. Pharm.*, 1922, **259**, 249; *A.*, ii, 538.

<sup>84</sup> A. Azadian, *Bull. Soc. chim. Belg.*, 1922, **31**, 15; *A.*, ii, 237.

<sup>85</sup> J. K. Rakshit, *Analyst*, 1921, **46**, 481; *A.*, ii, 96.

<sup>86</sup> H. E. Annett and M. N. Bose, *ibid.*, 1922, **47**, 387; *A.*, ii, 791.

<sup>87</sup> J. L. Morris and A. G. Macleod, *J. Biol. Chem.*, 1922, **50**, 55; *A.*, ii, 328.

<sup>88</sup> O. Folin and W. Denis, *ibid.*, 1913, **13**, 469; *A.*, 1913, ii, 162.

<sup>89</sup> G. Vortmann, *Boll. Sci. Tech.*, **3**, [No. 5]; *A.*, ii, 653.

<sup>90</sup> V. Macri, *Boll. Chim. farm.*, 1922, **61**, 417; *A.*, ii, 779.

<sup>91</sup> H. Ducloux, *Anal. Asoc. Quím. Argentina*, 1921, **9**, 215; *A.*, ii, 77.

<sup>92</sup> Lavoie, *J. Pharm. Belg.*, 1921, **3**, 889; *A.*, ii, 779.

by boiling with zinc powder) gives a pink coloration with a solution containing 1 part of copper in 100 millions.<sup>93</sup>

Bettendorff's test for arsenic (reduction with stannous chloride and hydrochloric acid), when applied as a microchemical test, is ten times as sensitive as the Marsh test; <sup>94</sup> and a solution of potassium thiocyanate will detect 1 part of osmium per million when shaken with the solution of the osmium salt and with ether, the ethereal layer assuming a blue coloration.<sup>95</sup>

A microchemical test for tungsten has been based on the formation of crystals of ammonium paratungstate when tungstic acid is treated with strong ammonia solution.<sup>96</sup>

For the detection of traces of uranium advantage has been taken of the fact that on treating a nitric acid solution of the metal with an excess of granulated zinc, a yellow deposit, apparently  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , is formed on the zinc.<sup>97</sup>

A reaction enabling magnesium to be separated from phosphate in an ammoniacal solution consists in the formation of the yellow insoluble compound,  $(\text{C}_9\text{H}_6\text{ON})_2\text{Mg} \cdot 4\text{H}_2\text{O}$ , on treating a suspension of magnesium hydroxide with an aqueous solution of 8-hydroxyquinoline sulphate. The precipitate, which forms characteristic micro-crystals, is given by a solution of 1 part of magnesium in 25,000.<sup>98</sup>

The sensitiveness of the various tests for strontium has been studied, and it has been found that the reaction with sulphuric acid is capable of detecting the smallest amount (1 : 125,000), the addition of alcohol increasing the sensitiveness to 1 : 1,400,000.<sup>99</sup>

Only a few new tests for kations have been published. These include one for fluorine, which consists in the formation of oily drops when the substance is heated at  $90^\circ$  with sand and sulphuric acid in a test-tube.<sup>1</sup>

*Quantitative.*—Numerous contributions have been published on the methods of determining hydrogen-ion concentration, and in particular on the applicability of various coloured indicators. The wide range, both in the acid and alkaline directions, of xylenol-blue recommends it as preferable to thymol-blue for chemical and biochemical work.<sup>2</sup> Phenol-red, on the other hand, is too

<sup>93</sup> P. Thomas and G. Carpentier, *Compt. rend.*, 1921, **173**, 1082; *A.*, ii, 86.

<sup>94</sup> H. Schenker, *Monatsh.*, 1921, **42**, 411; *A.*, ii, 526.

<sup>95</sup> M. Hirsch, *Chem. Ztg.*, 1922, **46**, 390; *A.*, ii, 459.

<sup>96</sup> J. A. M. van Liempt, *Z. anorg. Chem.*, 1922, **122**, 236; *A.*, ii, 787.

<sup>97</sup> H. D. Buell, *J. Ind. Eng. Chem.*, 1922, **14**, 593; *A.*, ii, 590.

<sup>98</sup> C. T. Mörner, *Pharm. Zentr.-h.*, 1922, **63**, 399; *A.*, ii, 659.

<sup>99</sup> O. Lutz, *Z. anal. Chem.*, 1921, **60**, 433; *A.*, ii, 227.

<sup>1</sup> B. Fetkenheuer, *Wiss. Veröff. Siemens-Konzern*, 1922, **1**, [3], 177; *A.*, ii, 655.

<sup>2</sup> A. Cohen, *Biochem. J.*, 1922, **16**, 31; *A.*, ii, 387.



greatly affected by the proportion of salts in the liquid to be a suitable indicator under all conditions.<sup>3</sup> In the case of sodium chloride and potassium chloride the corrections to be applied for a wide range of proportions of either salt have been ascertained for a number of indicators.<sup>4</sup>

By using mixtures of coloured salts (for example, ferric chloride and cobalt nitrate) in certain proportions as standards for the comparison of the colorations obtained with standard indicators, it is possible to determine the hydrogen-ion concentration without the use of buffer solutions.<sup>5</sup>

Greater accuracy is obtainable by the use of mixed indicators and titrating the liquid to a definite tint than is possible by taking the first colour change as the end-point of the titration.<sup>6</sup> An extended series of such mixed indicators, some of which are particularly suitable for use with coloured liquids, has been drawn up.<sup>7</sup>

In connexion with this part of the subject it may be mentioned that symmetrical diphenylguanidine has been suggested as an ideal acidimetric standard.<sup>8</sup>

A new acidimetric method of estimating copper depends on its precipitation as the salt,  $\text{CuSO}_4 \cdot 4\text{NH}_3$ , by means of alcohol, and titration of a solution of the precipitated salt with standard acid.<sup>9</sup>

Several new oxidimetric methods have been described. Thus, a rapid method of estimating chromium in nickel-chromium steel is based on its oxidation with potassium permanganate in sulphuric acid solution.<sup>10</sup>

A convenient method of estimating chlorine-ion in the presence of iodine-ion consists in precipitating them as silver salts and treating the precipitate with a measured excess of standard potassium ferrocyanide solution. This reacts only with the silver chloride, forming an insoluble silver potassium ferrocyanide, which is filtered off, and the excess of ferrocyanide titrated with permanganate.<sup>10</sup>

An oxidation method of estimating sulphides depends on the interaction of sodium sulphide and ferric sulphate and titration of the resulting ferrous sulphate with permanganate after neutral-

<sup>3</sup> A. Massink, *Pharm. Weekblad*, 1921, **58**, 1133; *A.*, ii, 307.

<sup>4</sup> I. M. Kolthoff, *Rec. trav. chim.*, 1922, **41**, 54; *A.*, ii, 222.

<sup>5</sup> *Idem*, *Pharm. Weekblad*, 1922, **59**, 104; *A.*, ii, 222.

<sup>6</sup> J. L. Lizius and N. Evers, *Analyst*, 1922, **47**, 331; *A.*, ii, 654.

<sup>7</sup> A. Cohen, *J. Amer. Chem. Soc.*, 1922, **44**, 1851; *A.*, ii, 780.

<sup>8</sup> C. A. Carlton, *ibid.*, 1469; *A.*, ii, 654.

<sup>9</sup> S. Minovici and A. Jonescu, *Bul. Soc. Chim. România*, 1921, **3**, 89; *A.*, ii, 162.

<sup>10</sup> G. B. Bonino, *Gazzetta*, 1921, **51**, ii, 261; *A.*, ii, 78.

isation with alkali carbonate.<sup>11</sup> In another oxidation method the sulphide is converted into sulphate by means of alkaline sodium hypobromite, the excess of which is estimated iodometrically.<sup>12</sup>

Dithionates resist the action of cold alkaline oxidising agents, and so may be differentiated from most other sulphur salts. They are decomposed, however, when heated with acid, and a method of estimating them is based on conducting the resulting sulphur dioxide into iodine solution.<sup>13</sup>

A solution of a bromate in strong hydrochloric acid will effect the quantitative oxidation of hydroxylamine and hydrazine, and the excess of bromate may be titrated. By then measuring the volume of nitrogen liberated from the hydrazine, the two substances can be estimated in the presence of each other.<sup>14</sup>

Further methods involving the use of cadmium as a reducing agent have been described.<sup>15</sup> For example, uranyl salts may be estimated by reduction with cadmium to uranous salts, followed by titration of the solution with permanganate. Vanadic acid is also quantitatively reduced.<sup>16</sup> In like manner, chlorates can be reduced to chlorides, and columbium estimated by reduction in a cadmium tube in the presence of ammonium molybdate or vanadate or of titanium sulphate, and subsequent titration with permanganate.<sup>17</sup>

Analogous use of liquid amalgams of cadmium and of zinc have also been described.<sup>18</sup> These can be used for the volumetric estimation of molybdenum, uranium, etc.,<sup>19</sup> for the reduction and differential titration of solutions containing two metals such as iron, titanium, or uranium, and for the estimation of chloric, bromic, and iodic acids.<sup>20</sup>

Metallic mercury is a suitable reducing agent for estimating vanadic acid in the presence of uranic and arsenic acids, which are not reduced by mercury.<sup>21</sup>

<sup>11</sup> P. P. Budnikoff and K. E. Krause, *Z. anorg. Chem.*, 1922, **122**, 171; *A.*, ii, 782.

<sup>12</sup> H. H. Willard and W. E. Cake, *J. Amer. Chem. Soc.*, 1921, **43**, 1610; *A.*, ii, 80.

<sup>13</sup> A. Fischer and W. Classen, *Z. angew. Chem.*, 1922, **35**, 198; *A.*, ii, 453.

<sup>14</sup> A. Kurtenacher and J. Wagner, *Z. anorg. Chem.*, 1921, **120**, 261; *A.*, ii, 312.

<sup>15</sup> Compare *Ann. Reports*, 1921, **18**, 158.

<sup>16</sup> W. D. Treadwell [with M. Blumenthal and with M. Hooft], *Helv. Chim. Acta*, 1922, **5**, 732; *A.*, ii, 788.

<sup>17</sup> W. D. Treadwell and others, *ibid.*, 806; *A.*, ii, 780.

<sup>18</sup> N. Kanô, *J. Chem. Soc. Japan*, 1922, **43**, 173; *A.*, ii, 519.

<sup>19</sup> *Idem*, *ibid.*, 333; *A.*, ii, 529.

<sup>20</sup> *Idem*, *ibid.*, 544; *A.*, ii, 721.

<sup>21</sup> L. R. W. McCay and W. T. Anderson, *J. Amer. Chem. Soc.*, 1922, **44**, 1018; *A.*, ii, 530.

The use of potassium ferrieyanide has been shown to give accurate results in the standardisation of thiosulphate solutions for iodometry.<sup>22</sup> A new iodometric method of estimating copper has been based on the oxidation of a cuprous salt with iodine, the excess of which is afterwards titrated. The copper is first converted into cuprous thiocyanate.<sup>23</sup> Hydrogen peroxide or nitric acid cannot be used for the oxidation of cuprous copper in presence of ferrous iron, and in such cases it is best to precipitate the iron from a hot ammoniacal solution by means of a current of air, and to use the filtrate, after removal of the ammonia, for the iodometric estimation of the copper.<sup>24</sup>

The influence of atmospheric oxygen in liberating iodine from hydriodic acid leads to erroneous results in the iodometric estimation of arsenic acid. It may be prevented by adding sodium hydrogen carbonate before the potassium iodide, and having only a minimum amount of hydrochloric or sulphuric acid present.<sup>25</sup>

Good results are obtained in the estimation of arsenic or antimony sulphide by treating their sodium hydroxide solution with iodine solution containing acetic acid and sodium acetate, and titrating the excess of iodine. Atmospheric oxidation is sufficiently checked by the addition of a small amount of gelatin.<sup>26</sup>

When a sulphur compound is heated with powdered iron in the absence of air, the whole of the sulphur is liberated as hydrogen sulphide, which may be collected in zinc sulphide solution and estimated iodometrically.<sup>27</sup>

Several new colorimetric methods have been devised. These include a method of estimating colloidal gold,<sup>28</sup> of estimating vanadium in steel by means of the coloration given by vanadium pentoxide with hydrogen peroxide,<sup>29</sup> of estimating manganese in steel and ores by oxidising it to the compound  $\text{H}_2\text{MnO}_3$ , an alkaline solution of which is yellowish-brown,<sup>30</sup> and of estimating antimony in copper.<sup>31</sup>

A colorimetric method of estimating phosphorus in steels is based on the blue coloration given by a hot solution of thiosulphate with ammonium phosphomolybdate,<sup>32</sup> and another method for phos-

<sup>22</sup> I. M. Kolthoff, *Pharm. Weekblad*, 1922, 59, 66; A., ii, 224.

<sup>23</sup> R. Lang, *Z. anorg. Chem.*, 1921, 120, 181; A., ii, 318.

<sup>24</sup> A. Wöber, *Z. angew. Chem.*, 1922, 35, 336; A., ii, 588.

<sup>25</sup> L. Rosenthaler, *Z. anal. Chem.*, 1922, 61, 222; A., ii, 584.

<sup>26</sup> F. Nikolai, *ibid.*, 257; A., ii, 585.

<sup>27</sup> L. Losana, *Giorn. Chim. Ind. Appl.*, 1922, 4, 204; A., ii, 582.

<sup>28</sup> J. A. Muller and A. Foix, *Bull. Soc. chim.*, 1922, [iv], 33, 717; A., ii, 662.

<sup>29</sup> A. Kropf, *Z. angew. Chem.*, 1922, 35, 366; A., ii, 590.

<sup>30</sup> J. Heslings, *Chem. Weekblad*, 1922, 19, 302; A., ii, 660.

<sup>31</sup> B. S. Evans, *Analyst*, 1922, 47, 1; A., ii, 231.

<sup>32</sup> L. Losana, *Giorn. Chim. Ind. Appl.*, 1922, 4, 60; A., ii, 392.

phorus on the coloration given by phosphates when boiled with ammonium vanadate and treated with ammonium molybdate.<sup>33</sup>

In separating arsenic from tungsten by volatilisation in a current of air at 100°, adsorption of arsenic trichloride may be prevented by bringing the tungstic acid into the disperse condition by treatment with pyrogallol (which is subsequently removed), or by adding glacial acetic acid prior to the addition of the hydrochloric acid and methyl alcohol.<sup>34</sup> Hydrolysis of the arsenic trichloride may be remedied by the addition of a salt, such as potassium bromide, which is readily soluble in water but dissolves with difficulty in strong hydrochloric acid. Successive small additions of concentrated hydrochloric acid will also prevent the hydrolysis.<sup>35</sup> In the presence of nitrites and nitrates the distillation method of estimating arsenic may give erroneous results, owing to the formation of nitrosyl chloride. This may be prevented by using hydrazine sulphate with sodium bromide as the reducing agent, and so simultaneously reducing nitrates, etc., to nitrogen.<sup>36</sup>

Minute quantities of arsenic may be quantitatively separated from germanium by treating the solution with a large excess of hydrofluoric acid prior to precipitation with hydrogen sulphide. Fluorogermanic acid is formed and is not precipitated by hydrogen sulphide.<sup>37</sup>

A quantitative estimation of manganese has been based on its precipitation as manganous iodate, which is dried at 100° and weighed.<sup>38</sup>

Selenium oxychloride has been used as a reagent for the separation of columbium and tantalum,<sup>39</sup> and for the separation of molybdenum trioxide from tungsten trioxide.<sup>40</sup>

Another method of separating small amounts of molybdenum from tungsten is to convert the molybdenum into xanthate, which can then be extracted with hot chloroform.<sup>41</sup>

Aluminium can be separated from iron by means of *o*-phenetidine, but the iron must be in the ferrous condition, since ferric salts give a precipitate with the reagent.<sup>42</sup>

<sup>33</sup> G. Misson, *Bull. Soc. chim. Belg.*, 1922, **31**, 222; *A.*, ii, 78.

<sup>34</sup> L. Moser and J. Ehrlich, *Ber.*, 1922, **55**, [B], 430; *A.*, ii, 314.

<sup>35</sup> *Idem*, *ibid.*, 437; *A.*, ii, 316.

<sup>36</sup> J. J. T. Graham and C. M. Smith, *J. Ind. Eng. Chem.*, 1922, **14**, 207; *A.*, ii, 314.

<sup>37</sup> J. H. Müller, *J. Amer. Chem. Soc.*, 1921, **43**, 2549; *A.*, ii, 320.

<sup>38</sup> S. Minovici and C. Kollo, *Chim. et Ind.*, 1922, **8**, 499; *A.*, ii, 787.

<sup>39</sup> H. B. Merrill, *J. Amer. Chem. Soc.*, 1921, **43**, 2378; *A.*, ii, 230.

<sup>40</sup> *Idem*, *ibid.*, 2383; *A.*, ii, 229.

<sup>41</sup> D. Hall, *ibid.*, 1922, **44**, 1462; *A.*, ii, 660.

<sup>42</sup> K. Chalupny and K. Breisch, *Z. angew. Chem.*, 1922, **35**, 263; *A.*, ii, 588.

A suitable method of estimating uranium has been based on its extraction from the mineral by means of a mixture of glacial acetic acid and nitric acid.<sup>43</sup>

### *Electrochemical Analysis.*

Among the apparatus for electrometric titration devised during the year mention may be made of a continuous-reading apparatus for the determination of hydrogen-ion concentration,<sup>44</sup> and of an apparatus in which the electrode vessel is attached to a rotating stirrer and carries a small bulb suitable for the preparation of a calomel electrode.<sup>45</sup>

It has been shown that errors in the conductometric method of precipitation are mainly due to excessive solubility of the precipitate, to the precipitate not being constant in composition, and to errors in determining the conductivity; and means of avoiding these errors have been pointed out.<sup>46</sup>

A simple method of electrometric titration for acidimetry or alkalimetry consists in the use of a number of constant and reproducible electrodes which are equivalent to hydrogen electrodes. These are especially useful when it is required to titrate a solution to an end-point of definite hydrogen-ion concentration.<sup>47</sup>

The use of a silver cathode with an anode of platinum alloyed with iridium or rhodium has been recommended for the rapid deposition of copper and zinc under specified conditions, and lead may be deposited as peroxide on the anode or as metal on the cathode according to the conditions of electrolysis.<sup>48</sup>

An iodine electrode may be conveniently used in numerous potentiometric estimations, such as the titration of iodides with silver nitrate, and the analysis of mercuric chloride, thalious salts, etc., but it is unsuitable for the estimation of lead or bismuth.<sup>49</sup> In most cases the end-point of a titration with silver nitrate is indicated by the solubility of the silver compound, and the method gives good results with chlorides, bromides, iodides, and many other salts.<sup>50</sup>

The use of lead nitrate in electrometric titration gives accurate results with iodides in the presence of chlorides and bromides, and for the estimation of certain organic salts.<sup>51</sup>

<sup>43</sup> W. W. Scott, *J. Ind. Eng. Chem.*, 1922, 14, 531; *A.*, ii, 788.

<sup>44</sup> H. Goode, *J. Amer. Chem. Soc.*, 1922, 44, 26; *A.*, ii, 307.

<sup>45</sup> C. A. Waters, *J. Soc. Chem. Ind.*, 1922, 41, 337T; *A.*, ii, 362.

<sup>46</sup> I. M. Kolthoff, *Z. anal. Chem.*, 1922, 61, 171; *A.*, ii, 452.

<sup>47</sup> P. F. Sharp and F. H. MacDougall, *J. Amer. Chem. Soc.*, 1922, 44, 1193; *A.*, ii, 579.

<sup>48</sup> A. Kling and A. Lassieur, *Ann. Chim. Analyt.*, 1922, 4, 171; *A.*, ii, 587.

<sup>49</sup> I. M. Kolthoff, *Rec. trav. chim.*, 1922, 41, 172; *A.*, ii, 388.

<sup>50</sup> *Idem*, *Z. anal. Chem.*, 1922, 61, 229; *A.*, ii, 581.

<sup>51</sup> *Idem*, *ibid.*, 369; *A.*, ii, 781.

Halogen-ions may also be accurately titrated with mercuric perchlorate, but only separately and not in admixture.<sup>52</sup>

When titrating ferrocyanides in acid solution with potassium permanganate solution, the end-point may be sharply obtained by an electrometric method,<sup>53</sup> but it is essential that sufficient acid, preferably hydrochloric acid, should be present to prevent the precipitation of manganese ferrocyanide.<sup>54</sup> On the other hand, when using ferrocyanide for the titration of certain metals, such as cadmium, zinc, or lead, the sharpness of the end-point is affected both by the insolubility of the resulting ferrocyanide of the heavy metal and by the nature of the alkali metal present.<sup>55</sup>

In the electrometric estimation of uranium by oxidimetric titration of the reduced uranium salt it is necessary to take into account that there are two changes in the oxidation potential, the first corresponding with the formation of quadrivalent, and the second with that of sexavalent uranium.<sup>56</sup>

An amalgam of zinc gives good results in the reduction of compounds of metals such as iron, molybdenum, vanadium, and uranium, prior to electrometric titration with potassium permanganate solution.<sup>57</sup> Another oxidimetric method consists in reducing a cupric salt with titanium trichloride and subsequently titrating the cuprous salt with standard dichromate or potassium bromate solution in an atmosphere of carbon dioxide.<sup>58</sup>

A series of test experiments has shown that traces of sulphate may be accurately estimated by conductometric titration with barium chloride, the addition of alcohol being an advantage.<sup>59</sup>

The conductometric method has also been applied to the titration of solutions of hydrofluosilicic acid,<sup>60</sup> to the titration of acids and phenol in alcoholic solution by means of an alcoholic solution of sodium ethoxide,<sup>61</sup> and to the titration of azo-dyestuffs and nitro-compounds.<sup>62</sup>

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<sup>52</sup> I. M. Kolthoff, *Z. anal. Chem.*, 1922, **61**, 332; *A.*, ii, 665.

<sup>53</sup> E. Müller and H. Lauterbach, *Z. anal. Chem.*, 1922, **61**, 398; *A.*, ii, 795.

<sup>54</sup> I. M. Kolthoff, *Rec. trav. chim.*, 1922, **41**, 343; *A.*, ii, 537.

<sup>55</sup> W. D. Treadwell and D. Chervet, *Helv. Chim. Acta*, 1922, **5**, 633; *A.*, ii, 786.

<sup>56</sup> D. T. Ewing and E. F. Eldridge, *J. Amer. Chem. Soc.*, 1922, **44**, 1484; *A.*, ii, 661.

<sup>57</sup> N. Kanô, *J. Chem. Soc. Japan*, 1922, **43**, 550; *A.*, ii, 721.

<sup>58</sup> E. Zintl and H. Wattenberg, *Ber.*, 1922, **55**, [B], 3366; *A.*, ii, 871.

<sup>59</sup> I. M. Kolthoff, *Z. anal. Chem.*, 1922, **61**, 433; *A.*, ii, 864.

<sup>60</sup> N. Kanô, *J. Chem. Soc. Japan*, 1922, **43**, 556; *A.*, ii, 719.

<sup>61</sup> E. R. Bishop, E. B. Kettridge, and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1922, **44**, 135; *A.*, ii, 308.

<sup>62</sup> D. O. Jones and H. R. Lee, *J. Ind. Eng. Chem.*, 1922, **14**, 46; *A.*, ii, 239.

## PHYSIOLOGICAL CHEMISTRY.

THE sad death of Benjamin Moore early in this year deprived Biochemistry of a brilliant and daring thinker. A pupil of Sir Edward Sharpey Schafer, he later was the first occupant of the chair of Biochemistry at Liverpool. While there, he and Mr. E. Whitley founded the *Biochemical Journal*, which, originally a private venture, later became the official publication of the Biochemical Society. A period of research on behalf of the Medical Research Council followed his resignation from Liverpool, but in 1920 he returned to academic life as first Professor of Biochemistry at Oxford. Unfortunately, his tenure of this post was for little more than a year. His loss as a teacher and an investigator is a severe one. The ranks of British men of science have been further depleted by the deaths of Dr. A. D. Waller, Professor of Physiology at London University, and the Hon. H. V. Onslow. Few who have read the valuable papers on biochemistry or genetics published from Onslow's Cambridge laboratory can have been aware that the whole of these careful researches were directed from an invalid's couch as the result of an accident in undergraduate days which paralysed him from the waist.

Amongst our foreign colleagues, we note with regret the loss of W. Palladin, the eminent Russian plant physiologist and biochemist, a pupil of Timiriazeff and latterly Professor at Petrograd; of Takamine, best known for his isolation of adrenalin; of C. A. Pekelharing, Emeritus Professor of Physiological Chemistry at Utrecht; and of Franz Hofmeister, the eminent investigator who for many years was Professor of Physiological Chemistry at Strassbourg.

Whilst the multiplication of new journals is generally to be deplored, we may perhaps except the *Journal of Biochemistry*, edited by Prof. Kakiuchi of Tokyo Imperial University, since it is obvious that the wide interest in biochemistry apparent in Japan should be served by a medium for home publication. The contents are published in English, German, and French. On the other hand, the appearance of the *Journal of Metabolic Research*, edited by F. M. Allen in the U.S.A., is, to our mind, less excusable. From a perusal of the papers in the numbers which have appeared there seems no adequate reason why existing periodicals should not have served for their publication. One fears that America is following the bad example of Germany in this matter.

Of the new books, attention must be directed to "Proteins and the Theory of Colloidal Behaviour," by Jaques Loeb, which deals in a remarkably clear manner with many problems of great import-

ance to biochemists. The great interest shown on all sides in the so-called vitamins is illustrated by the recent appearance of a large number of volumes dealing with these substances. Apart from the many more or less popularly-written books, amongst which special reference should be made to "Vitamins and the Choice of Food," by V. G. Plimmer and R. H. A. Plimmer, several valuable reviews with extensive bibliographies have been published. "The Vitamins," compiled by C. Sherman and S. L. Smith, and published by the American Chemical Society, is especially good, whilst a second edition of "Die Vitamine," by C. Funk, and an English translation of it by Dubin, are also welcome. Many new editions have also appeared; "Oxidations and Reductions in the Animal Body," by H. D. Dakin (2nd ed.); "The Determination of Hydrogen Ions," by W. M. Clark (2nd ed.); "Die Wasserstoffionenkonzentration, ihre Bedeutung für die Biologie und die Methoden ihrer Messung," by L. Michaelis, Part I (2nd ed., to be issued in three parts); "Les Colloïdes," by J. Duclaux (2nd ed.); and "Physikalische Chemie der Zelle und Gewebe," by R. Hober (5th ed., Part I). A valuable monograph on "Hexosamines, their Derivatives and Mucins and Mucoids," based on the author's researches, has been published from the Rockefeller Institute for Medical Research by P. A. Levene. The unwieldy "Handbuch der biologischen Arbeitsmethoden," edited by E. Abderhalden, continues to appear, but the later numbers are not such as will dispel the feeling of disappointment and irritation expressed by Professor Barger in his last year's Report. Two biographical studies have been published which are of interest to biochemists. "Pasteur and his Life," by Descour, is delightful and will share distinction with Vallery Radot's well-known book. On the other hand, a sense of disappointment may follow the perusal of the autobiography "Aus meinem Leben" of Emil Fischer, especially if one compares it with the very good biography by J. Kurt Hoesch which appeared in the pages of the *Berichte*. In connexion with the Pasteur Centenary, Masson et Cie are issuing an edition of the classical works of this master. The first two volumes, "Disymétrie moléculaire" and "Fermentations et générations dites spontanées," are about to appear.

#### *Amino-acids and Proteins.\**

No outstanding discovery marks this year's work in the field of protein chemistry, but steady progress can be reported. The diffi

\* Professor Barger has asked me to mention that in referring to the work of R. Willstätter and E. Waldschmidt Leitz (*Ber.*, 1921, 54, [B], 2988) in this section of his last year's Report he inadvertently omitted to state that F. W. Foreman had described a similar method previously (*Biochem. J.*, 1920, 14, 451).



culties of separating the products of hydrolysis of proteins make welcome the method described by H. W. Buston and S. B. Schryver,<sup>1</sup> which enables clean mixtures of amino-acids to be separated with ease from protein hydrolysates or other sources in a form convenient for further fractionation. A protein hydrolysate, after removal of tyrosine and the diamino-acids by the usual methods, is treated with baryta and alcohol, and carbon dioxide is passed. Several fractions of the barium salts of the carbamates of the amino-acids, having the general formula  $\text{RCH} \begin{smallmatrix} \text{NH}_3\text{CO}_3 \\ \text{CO}_2 \end{smallmatrix} \text{Ba}$ , ascribed by Siegfried,<sup>2</sup> may be obtained.

The barium precipitates on decomposition yield clean, semi-crystalline mixtures of amino-acids. It is claimed that the method will effect the quantitative removal of amino-nitrogen from a solution.

Another preliminary fractionation of the amino-acids which may eventually be of considerable value is described by G. L. Foster and C. L. A. Smith,<sup>3</sup> who apply on a laboratory scale the method of K. Ikeda and S. Susuki<sup>4</sup> in which a direct current is passed through a solution of the amino-acids, placed in a three-compartment cell. The units which are predominantly acid, such as glutamic acid, migrate to the anode, the basic substances, lysine, arginine, etc., travel to the cathode, and the more or less neutral units remain in the central compartment. The method appears to yield relatively large amounts of clean preparations of arginine and lysine.

R. Engeland<sup>5</sup> has described a method in which the monoamino-acids are converted into the corresponding betaines as a means of estimating certain units. From elastin he has isolated the betaine of what he believes to be a hitherto unknown amino-acid with the formula  $\text{C}_{13}\text{H}_{26}\text{O}_4\text{N}_2$ .

The general feeling that our knowledge of the sulphur-containing constituents of the proteins is lamentably deficient is reflected in several papers. Of particular interest is the announcement by J. H. Mueller<sup>6</sup> of his isolation of a new amino-acid containing sulphur from the products of hydrolysis of commercial caseinogen with sulphuric acid. Further details of this acid will be awaited with great interest, but the preliminary communication states that there are indications that it is a straight-chain compound with two amino-groups and probably two carboxyl groups. It is uncertain in what form the sulphur is present. W. F. Hoffmann and R. A. Gortner<sup>7</sup>

<sup>1</sup> *Biochem. J.*, 1921, 15, 636; *A.*, 1921, i, 182.

<sup>2</sup> *Z. physiol. Chem.*, 1905, 46, 401; *A.*, 1906, i, 324.

<sup>3</sup> *Proc. Soc. Exp. Biol. Med.*, 1922, 19, 348.

<sup>4</sup> *U.S. Pat.* 1015891, 1912.

<sup>5</sup> *Z. physiol. Chem.*, 1922, 120, 130; *A.*, ii, 536.

<sup>6</sup> *Proc. Soc. Exp. Biol. Med.*, 1922, 19, 161.

<sup>7</sup> *J. Amer. Chem. Soc.*, 1922, 44, 341; *A.*, i, 429.

have studied the effect of acid hydrolysis on cystine and report interesting observations. Pure cystine, boiled for varying lengths of time with 20 per cent. hydrochloric acid, underwent only slow decomposition, and the authors do not think there is appreciable decomposition of cystine during the usual protein hydrolysis. The small amount of sulphur liberated was either in the form of hydrogen sulphide or of free sulphur. The cystine after hydrolysis showed certain differences from the original product in being less readily precipitated by phosphotungstic acid, optically inactive, more soluble in water, and crystallising in prisms. The derivatives of the two forms of cystine showed dissimilarities. The authors advance the suggestion that the isomeric cystine they have isolated is identical with the synthetic product of Erlenmeyer and Stoop<sup>8</sup> and of Fischer and Raske,<sup>9</sup> and that "plate" cystine as obtained from the hydrolysis of proteins has never been synthesised.

The unsatisfactory nature of the existing methods for the analysis of the diamino-acid fraction of protein hydrolysates is apparent to all who have had occasion to use them. Recently J. L. Rosedale,<sup>10</sup> in an investigation of the diamino-acid content of muscle proteins, has referred to the inconsistencies of the results obtained by the well-known method of Van Slyke.

The inaccuracies associated with the estimation of the acids in this fraction are largely bound up with those due to the method of determining arginine, as pointed out by R. H. A. Plimmer,<sup>11</sup> who also modified the process to render it somewhat more trustworthy. Even when there is reason to believe that the estimation of arginine is satisfactory, the value for histidine, and therefore indirectly that for lysine, is based on the assumption that the whole of the non-amino-nitrogen of the fraction is represented by histidine and arginine. That this assumption is liable to lead to serious error is now definitely proven by the investigations of D. D. Van Slyke and A. Hiller.<sup>12</sup> They found that the values for histidine obtained by the usual method and those based on K. K. Koessler and M. T. Hanke's<sup>13</sup> colorimetric process show agreement in the case of caseinogen, edestin, and fibrin, but a considerable difference with gelatin. This led them to fractionate the phosphotungstic acid precipitate obtained from hydrolysed gelatin, as a result of which evidence was obtained of the presence of an unidentified base. Attempts to obtain the free base in a crystalline condition

<sup>8</sup> *Ber.*, 1908, **41**, 893; *A.*, 1908, **i**, 325.

<sup>9</sup> *Annalen*, 1904, **337**, 222; *A.*, 1905, **i**, 119.

<sup>10</sup> *Biochem. J.*, 1922, **16**, 27; *A.*, **i**, 492.

<sup>11</sup> *Ibid.*, 1916, **10**, 115; *A.*, 1916, **ii**, 460.

<sup>12</sup> *Proc. Nat. Acad. Sci.*, 1921, **7**, 185; *A.*, **i**, 63.

<sup>13</sup> *J. Biol. Chem.*, 1919, **39**, 497; *A.*, 1920, **ii**, 67.

were unsuccessful. It is hygroscopic, decomposes slowly at  $100^{\circ}$ , and has a ratio of nitrogen to amino-nitrogen of 2:1. As the value remains constant after treatment with acids, it is concluded that the substance is not a peptide. Further information of this new basic constituent of the proteins will be awaited with great interest.

The presence of hydroxyaspartic acid among the products of hydrolysis of proteins once reported by Z. H. Skraup<sup>14</sup> has not been confirmed by a careful examination of the products of tryptic digestion of caseinogen by H. D. Dakin.<sup>15</sup> Further study of this acid has, however, been facilitated by his synthesis of the para- and anti-hydroxyaspartic acids from chloromalic acid and ammonia. Separation of the isomerides was effected by fractional crystallisation, whilst in a later paper<sup>16</sup> is described the resolution of the anti-acid by means of the strychnine and quinine salts. The para-acid was not resolved.

Gradually, but very slowly, information on the difficult problem of the mode of linking of the amino-acids in proteins is being collected, but it is somewhat surprising that a comparatively simple class such as the protamines has not been the subject of more extensive study from this point of view. R. E. Gross<sup>17</sup> has, however, isolated from the products of hydrolysis of clupeine a dipeptide-like substance consisting of at least two arginine molecules. He has also confirmed Nelson Gerhardt's<sup>18</sup> deduction that in salmine and clupeine the monoamino-acids are linked together. Clupeine has also been investigated by H. Steudel and E. Peiser,<sup>19</sup> who have prepared combinations of the protamine with guanylic acid and yeast-nucleic acid in an attempt to elucidate the constitution of the nucleo-proteins. E. Abderhalden<sup>20</sup> has succeeded in isolating at intermediate stages in the hydrolysis of silk fibroin considerable quantities of a *d*-alanyl-glycine anhydride and small quantities of glycyl-*l*-tyrosine anhydride, and of a compound containing serine, *d*-alanine, and glycine. Incidentally his examination of this protein accounted for 86.4 per cent. of the total amino-acids as compared with previous figures in the neighbourhood of 70 per cent. The current idea that the free amino-nitrogen of proteins is related to the lysine content receives support from the

<sup>14</sup> *Ber.*, 1904, **37**, 1596; *A.*, 1904, i, 538.

<sup>15</sup> *J. Biol. Chem.*, 1921, **48**, 273; *A.*, i, 143.

<sup>16</sup> *Ibid.*, 1922, **50**, 403; *A.*, i, 430.

<sup>17</sup> *Z. physiol. Chem.*, 1922, **120**, 167; *A.*, i, 784.

<sup>18</sup> *Ibid.*, 1919, **105**, 165; *A.*, 1919, i, 503.

<sup>19</sup> *Ibid.*, 1922, **120**, 207; *A.*, i, 784.

<sup>20</sup> *Ibid.*, 1922, **122**, 298; *A.*, i, 1200.

work of M. S. Dunn and H. B. Lewis,<sup>21</sup> who have studied the distribution of nitrogen in caseinogen and deaminised caseinogen. Lysine was found to be absent from the products of the hydrolysis of the deaminated protein and some destruction of tyrosine had also occurred. In a later paper,<sup>22</sup> they record that the deaminated caseinogen can be hydrolysed by pepsin and trypsin, but at a slower rate than in the case of the untreated protein, whilst experiments on a dog indicate that, when tolerated, it can also be metabolised by the organism.

### *Protein Metabolism.*

At least one outstanding paper on protein metabolism has appeared during the twelve months under review. This is the paper by C. J. Martin and R. Robison<sup>23</sup> on the minimum nitrogen expenditure of man and the biological value of various proteins for human nutrition. Its appearance marks a very important advance in this branch of the science of nutrition. The realisation that the proteins do not have a uniform value in nutrition was gaining ground at the close of the last century, and was, indeed, definitely formulated by Rubner in 1897, but the term "biological value" which is to-day so widely employed in this connexion was introduced by Karl Thomas<sup>24</sup> in 1909. This investigator defined the "biological value" of a protein as the number of parts of body nitrogen replaceable by 100 parts of the nitrogen of the foodstuff, and the values he determined have been extensively employed by physiologists. Martin and Robison began their investigation with the modest object of redetermining the relative values for certain cereal proteins, but they soon found great difficulty in arriving at values which could justifiably be compared and began to suspect that a number of the earlier investigations were open to criticism. Accordingly, they began a careful investigation of the conditions under which valid results might be obtained, and their paper represents not only a sound criticism of earlier determinations, but also a most valuable study of the experimental methods concerned. They point out that Thomas adopted an experimental method based on the assumption that the value of any protein for biological purposes remains uniform whatever the amount taken. The misleading nature of this procedure can best be appreciated if the case of gelatin is considered. The various possibilities are explained by the authors by means of the diagram reproduced on p. 188, in which the abscissæ represent real nitrogen intake and the

<sup>21</sup> *J. Biol. Chem.*, 1921, **49**, 327; *A.*, i, 279.

<sup>22</sup> *Ibid.*, **343**; *A.*, i, 292.

<sup>23</sup> *Biochem. J.*, 1922, **16**, 407.

<sup>24</sup> *Arch. Physiol.*, 1909, 219.

ordinates real nitrogen output. If  $OM = m$  represent the output of nitrogen on a nitrogen-free diet of adequate fuel value, then  $m$  is equal to the nitrogen minimum.

The administration of an ideal protein (biological value 100, and utilised without waste) in gradually increasing amounts will result in no change in the amount of excreted nitrogen,  $m$ , until the intake equals that value, at which point,  $E$ , where  $ME = MO$ , the body will be in nitrogen equilibrium. When the intake rises above  $m$ , the graph of intake and output will follow the line  $EE_n$  at an angle of  $45^\circ$  to the axis (unless the body is growing or has pre-

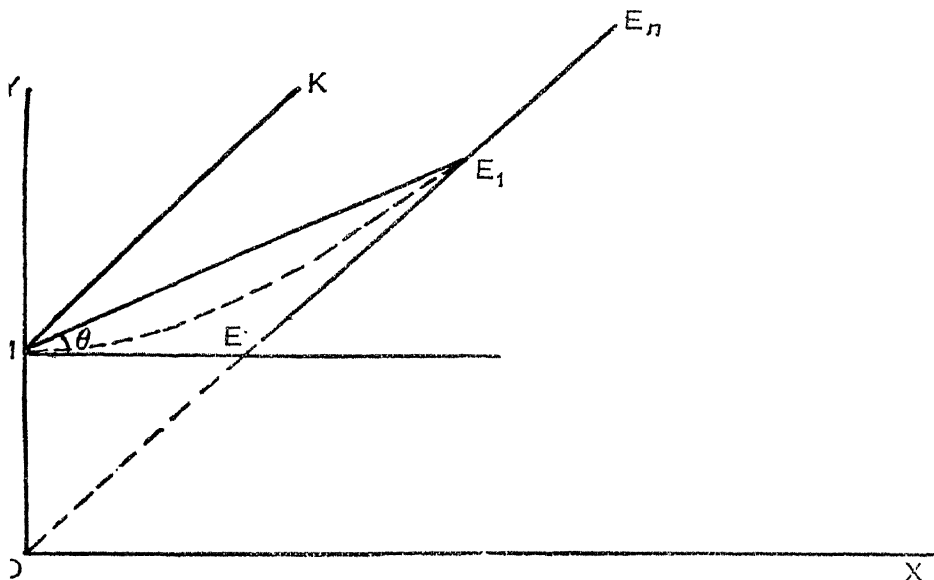


FIG. 1.

viously been starved of nitrogen). Ordinary proteins with biological values less than 100 will not suffice for equilibrium to be established at the point  $E$ , but at some other point  $E_1$ . Before nitrogen equilibrium is reached, the graph will follow the line  $ME_1$ , which may be either straight or curved, depending on the indivisibility of the nitrogen requirements of the body and the uniform economy with varying nitrogen intake. If these conditions are obtained, then Thomas's formula,

$$BV = 100 \frac{\text{Urine N on N-free diet} + \text{faeces N} + \text{balance}}{\text{N intake}},$$

becomes  $BV = 100 (1 - \tan \theta)$ .

In the case of a protein inadequate to supply any portion of the requirements of the organism, the graph will be the line  $MK$  parallel

to  $OE_n$ ; that is, the nitrogen output will always equal the nitrogen intake plus the value  $m$ . That is,  $BV = 100 (1 - \tan 45^\circ) = 0$ .

Whilst there was very little reason for assuming that these graphs would prove to be straight lines, the experimental determination of a number of points at different levels of intake of the same protein demonstrated that in the case of bread approximation to a straight line actually occurs. There was evidence that this may be also true for milk proteins. In the case of gelatin, however, the ratio certainly does not remain constant, and there is no indication that the amount of body nitrogen saved increases beyond that effected by the smallest amount of gelatin administered. It can therefore be seen that the application of Thomas's method is justifiable in the case of bread, doubtful with milk, and of no value in the case of gelatin. In cases where his method is not known to be trustworthy, the ratio body-N saved/food-N absorbed should be determined close to, but below, the point of equilibrium. In any case, the biological values derived from experiments of comparatively short duration have a limited significance. The value of gelatin in relation to the nitrogen requirements of man is also very fully treated in an interesting paper by R. Robison<sup>25</sup>; these researches have in addition served to provide further information regarding the distribution of nitrogen in the urine on diets low in nitrogen.<sup>26</sup>

#### *Glutathione and Tissue Oxidations.*

Reference was made in last year's Report to the discovery by Hopkins of an auto-oxidisable constituent of the cell, and further information regarding this remarkable substance has since been eagerly awaited. Late in the year our expectations were fulfilled by the appearance of a publication by F. G. Hopkins and M. Dixon.<sup>27</sup> This paper is concerned with significance of glutathione in the oxidative mechanisms of the cell, but chemists will welcome the statement that a full study of the chemical properties of this substance is in progress. It should not be a task of excessive difficulty to establish the mode of linking between the constituent amino-acids, cystine and glutamic acid, as a first step towards synthesis. The most striking fact reported in the new paper from the Cambridge laboratory is the apparent association, in oxidative and reductive processes, of the dipeptide with a tissue agency which is insoluble in water and resistant to a temperature of  $100^\circ$ , or to treatment with alcohol. It will be recalled that O. Meyerhof,<sup>28</sup> in 1918, demonstrated

<sup>25</sup> *Biochem. J.*, 1922, **16**, 111; *A.*, i, 488.

<sup>26</sup> *Ibid.*, 131; *A.*, i, 495.

<sup>27</sup> *J. Biol. Chem.*, 1922, **54**, 527.

<sup>28</sup> *Arch. Ges. Physiol.*, 1918, **170**, 428.

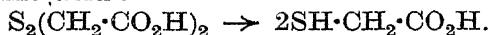
that the ability of a yeast extract or "Kochsaft" to give the nitroprusside reaction showed a certain parallel with its power to restore the "respiration" of washed acetone yeast. His investigations showed that cystine had not the latter effect, but when thioglycollic acid or thiolactic acid was added to the washed yeast in a neutral or slightly acid medium, oxygen was absorbed in an amount larger than that required to oxidise the added acid to the disulphide form. Furthermore, Meyerhof demonstrated the even more remarkable fact that a similar action follows the addition of thioglycollic acid to a washed yeast which has been heated at 100°.

The parallel between Meyerhof's results and those now recorded by Hopkins and Dixon is at first sight a close one, but more detailed examination of the experimental data indicates that further information is necessary before a definite opinion on this point can be formed. The experiments at the Cambridge laboratory once again demonstrate how valuable may be the information obtained by the study of tissue activities before and after they have been thoroughly extracted to remove water-soluble components. By this means assistance in recognising the co-ferment of alcoholic fermentation was obtained by Harden and Young, whilst more recently both Meyerhof and Batelli and Stern have used this method with considerable success in their attempts to elucidate the nature of the oxidative mechanisms in the living cell. In Hopkins and Dixon's experiments it was found that fresh muscle-tissue, after being thoroughly washed, does not reduce methylene-blue, or reduces it very slowly, nor will such tissue show the absorption of oxygen and liberation of carbon dioxide which are characteristic of respiration. The addition of glutathione, which is, of course, one of the soluble constituents removed by the washing, to the washed tissue, suspended in a "buffered" phosphate solution, will not only restore the power to reduce methylene-blue, but also will enable the tissue to "respire." The most interesting point is, however, that the power to reduce the dye and to show respiration on addition of glutathione is displayed, not only by the washed tissue, but also by tissue which has been extracted thoroughly with boiling water or alcohol or which has been heated at 100°.

That the thermostable agent in the tissue residues shows a definite reducing power is demonstrated by the prompt reduction of the added oxidised form of glutathione, enabling the system to show reduction of methylene-blue or "respiration." The tissue residues must therefore contain a stable hydrogen donator, which is relatively insoluble in water, and presumably some form of stable primary catalytic system for which glutathione is a co-agent. The thermostable tissue factor activated by glutathione is sensitive to oxidation,

presumably owing to the slow oxidation of the relatively labile hydrogen atoms which in the normal system are so readily yielded to other acceptors. Even the transport of the labile hydrogen to atmospheric oxygen is accelerated by glutathione, and in this case the absorption of oxygen may be as much as 400 c.c. of oxygen per gram of dried material. This amount appears to be, from the approximate data available, about one-tenth of the total possible uptake of the original untreated tissue. The respiratory exchange of this process is about unity in the early stages, but falls off after a time to nearly zero. Hopkins and Dixon's paper contains a careful discussion of glutathione in relation to other systems of oxidative mechanism which are believed to exist. The molecule of glutathione is not oxidised anaërobically by washed tissues in the presence of methylene-blue as T. Thunberg<sup>29</sup> found was the case with such substances as succinic acid and glutamic acid. Moreover, it does not suffer oxidation by atmospheric oxygen as a result of surface action such as occurred in the case of certain amino-acids in the presence of charcoal studied by Warburg.<sup>30</sup> Apparently the molecule of the dipeptide is stable, apart from the reversible change of the sulphur groupings which is its main characteristic. So far as the authors can ascertain, glutathione takes no part in such oxidising agencies as are associated with the "oxydases" present in the cold-water extracts of tissues. The nature of the oxidation-reduction systems existing in washed tissues still requires a good deal of elucidation, but it is quite clear that the thermolabile and unstable factors which are probably responsible for the effects observed by Thunberg (the "oxydones" of Batelli and Stern<sup>31</sup>) are distinct from the thermostable factors described by Hopkins and Dixon and by Meyerhof. It is rather in relation to the "respiratory substance" (Atmungskörper) and the oxidising system described by the latter investigator that glutathione must be considered, and H. D. Dakin,<sup>32</sup> for one, has suggested that Meyerhof's activator to respiratory activity in killed washed yeast may be none other than the new dipeptide.

The experiments of Meyerhof on the power of thioglycollic acid to restore the "respiration" of killed, washed yeast are of great interest in the light of Hopkins and Dixon's observations that washed tissues actually have the power to effect the reduction of dithiodiglycollic acid:



<sup>29</sup> *Skand. Arch. Physiol.*, 1920, 40, 1; *A.*, 1920, i, 784.

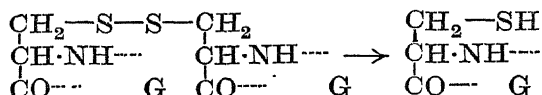
<sup>30</sup> *Biochem. Z.*, 1921, 113, 257; *A.*, 1921, i, 230.

<sup>31</sup> "Ueber den Mechanismus der Oxydationsvorgänge im Tierorganismus," Jena, 1914.

<sup>32</sup> *Physiol. Rev.*, 1922, 1, 394.



Dithiodiglycollic acid promotes oxygen transport less effectively than does oxidised glutathione in the change.



If the conception of the "Atmungskörper" be such that it is regarded as representing the action of two or more substances each related to some particular aspect of respiratory oxidation, then glutathione is one of these, its activity being mainly relative to respiratory factors which are thermostable. We may perhaps quote an extract from the paper by Hopkins and Dixon: "The facts suggest that coexisting in living tissues with the special enzymic mechanism is a thermostable mechanism for oxidations and reductions. Materials in close association with structural elements are oxidised, aëroically or anaëroically, with the coagency of the sulphur groups of glutathione." The nature of the thermostable agent or agents residual in the washed tissues is as yet undiscovered.

#### *Mammary Secretion.*

A study of the origin of milk fat and its relation to the metabolism of phosphorus has been made by J. Sheehy,<sup>33</sup> who finds that carbohydrate and fat can replace each other in the diet for the manufacture of fat by the mammary gland. His conclusion that the immediate precursor is a diffusible substance of the nature of a phosphatide constitutes further support for the work of E. B. Meigs, N. R. Blatherwick, and C. A. Carey,<sup>34, 35</sup> who showed that the increase in inorganic phosphate after the blood has passed through the mammary gland is sufficient to account for the whole of the milk fat having been formed from a precursor of that type. The significance of phosphorus in the transport of fat in the animal body is also emphasised by Bloor in a useful review of the subject.<sup>36</sup>

The significance of colostrum remains obscure. J. H. Lewis and H. G. Wells<sup>37</sup> regard it as a source from which the young derive the specific anti-bodies of the maternal organism which are believed to be associated with the globulin fraction. Support for this view may perhaps be derived from the experiments of T. Smith and R. B. Little,<sup>38</sup> who found that calves are more liable to succumb to

<sup>33</sup> *Biochem. J.*, 1921, **15**, 703.

<sup>34</sup> *J. Biol. Chem.*, 1919, **37**, 1; *A.*, 1920, **i**, 203.

<sup>35</sup> *Ibid.*, 1920, **40**, 469.

<sup>36</sup> *Physiol. Rev.*, 1922, **2**, 92.

<sup>37</sup> *J. Amer. Med. Assoc.*, 1922, **78**, 863.

<sup>38</sup> *J. Exper. Med.*, 1922, **36**, 181.

bacterial invasion when they are deprived of colostrum. Whether this protective action is directly due to anti-bodies or indirectly to a strengthening of the resistant powers of the organism by other factors is not yet clear, but it must be recalled that colostrum is richer than ordinary milk in vitamin-*A*, and that there is a good deal of evidence that this substance assists to maintain the defence of the body's tissues.<sup>39</sup> It would now seem to be established with some certainty that the diet of the lactating female is the chief factor determining the concentration of vitamins in the milk, but the paper by C. Kennedy and R. A. Dutcher<sup>40</sup> is important because it proves that the vitamin value of the milk of cows can be maintained throughout the winter period of stall feeding by care in the selection of a ration consisting of a proper balance between grains and leafy foods. The far-reaching influence of the diet of the mother on the nutritive value of the milk is further illustrated by the experiments of G. Hartwell. In a study of the effect of diet on mammary secretion,<sup>41</sup> she investigated the effect of changing the balance of the chief food components, and discovered that an excess of protein tends to cause an interference with the normal lactation leading to nutritional disturbances in the young. Further experiments<sup>42, 43</sup> confirmed this observation, but the cause of this effect of the protein has not yet been ascertained with certainty. Apparently the high protein diet is not in itself deleterious, a view supported by the results of J. C. Drummond, G. P. Crowden, and E. L. G. Hill,<sup>44</sup> but it seems to demand a readjustment in the balance of certain other food units. The beneficial influence of a supplement of fresh milk or marmite (commercial yeast extract) led to suggestions being advanced that the vitamin-*B* may be the factor concerned,<sup>44, 45</sup> and further researches by Hartwell appear to confirm this view.<sup>46</sup> In continuance of her studies on the influence of proteins on mammary secretion, Miss Hartwell has been unable to obtain evidence that edestin possesses any specific action as a galactagogue.<sup>47</sup>

#### *Sugar Metabolism and Diabetes.*

The mechanism by which dextrose is broken down in the animal body is a subject which continues to attract widespread interest.

<sup>39</sup> Drummond, Coward, and Watson, *Biochem. J.*, 1921, **15**, 540.

<sup>40</sup> *J. Biol. Chem.*, 1922, **50**, 339.

<sup>41</sup> *Biochem. J.*, 1921, **15**, 141.

<sup>42</sup> *Ibid.*, 563.

<sup>43</sup> *Ibid.*, 1922, **16**, 78.

<sup>44</sup> *J. Physiol.*, 1922, **56**, 413.

<sup>45</sup> C. Kennedy and L. S. Palmer, *J. Biol. Chem.*, 1922, **54**, 217.

<sup>46</sup> *Biochem. J.*, 1922, **16**, 825.

<sup>47</sup> *Lancet*, 1921, **i**, 323.

There is a tendency at the moment, however, for chief attention to be transferred from the intermediate stages, in which the hexose molecule is degraded, to the elucidation of the changes which are believed to occur before the sugar molecule is actually broken.

The researches of Embden and his co-workers<sup>48</sup> have made it appear probable that phosphorus compounds are concerned in the early stages of the metabolism of hexoses, and his conception of the rôle of hexosephosphoric acid in the molecule of the "lactacidogen" complex presents an interesting parallel with the current views on the significance of this acid in the fermentation of sugars by yeast. D. L. Foster and D. M. Moyle<sup>49</sup> have recently found that chopped muscle not only has the power to break down added hexosephosphate *in vitro*, but also has the ability to synthesise that complex from dextrose and phosphoric acid. On all hands, evidence is accumulating that the hexose molecule, before it can be broken down in the normal manner by living cells, must pass through the state of hexosephosphate, and there can be little doubt that during this process a rearrangement of the molecule occurs with the production of a highly reactive form of the sugar.

The rôle of phosphates in the oxidation of hexoses in the living cell has led A. Harden and F. R. Henley<sup>50</sup> to examine the significance of these salts in the oxidation of dextrose by hydrogen peroxide. W. Löb and his co-workers<sup>51</sup> believe that the oxidation depends on the hydroxyl-ion concentration and that phosphates exert a specific accelerating effect on the reaction. This view was supported by Witzemann,<sup>52</sup> who further suggested that the specific action of the phosphates might be attributable to the necessity of the intermediate formation of a hexosephosphate. Harden and Henley's investigations show, however, that the action of phosphates in this oxidation is not specific, but that it depends on their power to regulate the reaction of the medium. Other "buffer" systems were equally effective. H. Elias and St. Weiss<sup>53</sup> have found that intravenous injections of sodium mono- and di-phosphates may lower both alimentary and diabetic hyperglycæmia, but they do not influence the level of blood-sugar in normal subjects. It is suggested that in the former cases either the combustion of dextrose is stimulated or that storage of hexose, possibly as a phosphoric acid complex, may occur.

<sup>48</sup> *Z. physiol. Chem.*, 1914, **93**, 1, 94, 124; *A.*, 1915, i, 344, 345, 346.

<sup>49</sup> *Biochem. J.*, 1921, **15**, 672; *A.*, i, 398.

<sup>50</sup> *Ibid.*, 1922, **16**, 143; *A.*, i, 433.

<sup>51</sup> *Biochem. Z.*, 1911, **32**, 43; 1912, **46**, 288; 1915, **68**, 368; *A.*, 1911, ii, 504; 1913, i, 125; 1915, ii, 247.

<sup>52</sup> *J. Biol. Chem.*, 1920, **45**, 1; *A.*, 1921, i, 160.

<sup>53</sup> *Weiner. Arch. inn. Med.*, 1922, **4**, 29; *A.*, i, 1085.

Speculation as to the reactive form of sugar produced by the hypothetical preliminary rearrangement is already active. A. Bornstein and K. Holm <sup>54</sup> believe it to be lævulose or a related substance, but probably more support is to be given to the suggestion that it is the reactive ethylene-oxide form of dextrose. J. A. Hewitt and J. Pryde <sup>55</sup> have already presented evidence that solutions of dextrose and lævulose in contact with the mucous membrane of the intestine are converted into  $\gamma$ -glucose. Such views have led to a re-examination of the nature of the reducing substances of the blood by E. A. Cooper and H. Walker. <sup>56</sup> They have found that dextrose is the chief reducing substance present, but that other reducing substances of a more complex nature are occasionally detectable. They obtained no evidence, however, that human blood can transform dextrose or lævulose into the highly reactive ethylene-oxide forms, an observation which confirms the results of J. A. Hewitt and D. H. de Souza. <sup>57</sup>

More recently still, L. B. Winter and W. Smith <sup>58</sup> have definitely advanced the opinion that the sugar present in normal blood is an unstable form of glucose of low initial rotatory power and possibly the so-called  $\gamma$ -glucose or ethylene oxide form of dextrose. This view is based on their observations that in the protein-free filtrates of normal blood the copper-reducing values and those obtained by polarimetric determinations at first show disagreement, but after some time, two to three days, the values in the latter case gradually approach the former until agreement is reached. In the case of diabetic bloods, however, the polarimetric readings gave higher values than the copper method; but here again, after a period of time, agreement between the two determinations was obtained.

It is suggested that the blood-sugar in cases of diabetes is the  $\alpha$ -  $\beta$ -dextrose and that the failure of the organism to utilise sugar in this disease is due to the absence or inactivity of an enzyme which in the normal subject converts the  $\alpha$ - and  $\beta$ -sugars into the active  $\gamma$ -form. Their suggestions are of very great interest and may lead to results of the highest importance, but the evidence on which they are advanced is far from being as convincing as might be desired.

The inability of the diabetic organism to utilise dextrose has for a long time been associated with a disturbance of the internal secretion of the pancreas. The classical researches of von Mering

<sup>54</sup> *Biochem. Z.*, 1922, **130**, 209; *A.*, i, 890.

<sup>55</sup> *Biochem. J.*, 1920, **14**, 395; *A.*, 1920, i, 508.

<sup>56</sup> *Ibid.*, 1921, **15**, 415; *A.*, i, 698.

<sup>57</sup> *Ibid.*, 667; *A.*, i, 395.

<sup>58</sup> *J. Physiol.*, 1922, **57**, 100.

and Minkowski<sup>59</sup> demonstrated that a condition closely resembling human diabetes mellitus may be established in dogs by complete extirpation of the pancreas.

This led Lepine<sup>60</sup> to suggest that the condition is due to the withdrawal of an internal secretion of the pancreas which is essential for the utilisation of sugar. Many attempts have since been made to demonstrate the existence of a pancreatic hormone, chiefly by the administration of extracts prepared by various means from the gland,<sup>61, 62, 63, 64, 65</sup> but although occasionally evidence was obtained of an improved utilisation or of a temporary reduction of the sugar output, the results were never conclusive. The cause of the uncertain activity of the preparations was not definitely ascertained, but by some it was considered to be the destructive action of trypsin. These views, together with pathological evidence that the islets of Langerhans frequently show atrophy in cases of diabetes, have led two young Canadian clinicians, F. G. Banting and C. H. Best, of Toronto, to investigate the action of extracts of the islets alone in the treatment of experimental diabetes in dogs. This was attained by preparing extracts either from foetal glands, in which only the islet tissue was present, or from glands in which atrophy of the other parts of the structure had been induced by ligature of the pancreatic duct. The administration of these extracts to diabetic dogs was found to bring about a very marked fall in the blood- and urinary- sugar and to improve the general condition of the animals in a most striking manner.<sup>66</sup> Encouraged by their success, they proceeded to attempt the extraction of the active substance from normal ox pancreas, using alcohol as a means of preventing enzyme action, a method previously employed by Scott.<sup>62</sup> The material thus prepared proved so potent in the treatment of dogs that it was tried in a severe case of diabetes in a boy of fourteen. The result was a reduction of the blood-sugar by 25 per cent.<sup>67</sup>

To the active substance present in these extracts the discoverers give the name "insulin." By mobilising a team of research workers, the Toronto investigators have in a remarkably short time reported a considerable progress in the study of this new substance. The

<sup>59</sup> *Arch. exp. Path. Pharm.*, 1889, **31**, 371.

<sup>60</sup> "Le diabète sucre," Paris, 1909.

<sup>61</sup> Starling and Knowlton, *J. Physiol.*, 1912, **45**, 146.

<sup>62</sup> E. L. Scott, *Amer. J. Physiol.*, 1912, **29**, 3.

<sup>63</sup> J. R. Murlin and B. Kramer, *J. Biol. Chem.*, 1913, **15**, 365.

<sup>64</sup> Kleiner, *ibid.*, 1919, **40**, 153.

<sup>65</sup> Clarke, *Johns Hopkins Hosp. Rep.*, 18, 229.

<sup>66</sup> *J. Lab. Clin. Med.*, 1922, **7**, 251.

<sup>67</sup> *Ibid.*, 260.

method of preparation has been improved by J. B. Collip,<sup>68</sup> whose process, now generally employed, is a prolonged and rather laborious fractionation by means of alcohol.

The administration of insulin not only reduces the hyperglycæmia in diabetes, but also that associated with sugar puncture, adrenalin, or ether anæsthesia,<sup>69</sup> which may help to explain the observations of L. Adler<sup>70</sup> that the simultaneous administration of pancreatic extract, made from hibernating hedgehogs, more or less completely suppresses the action of adrenalin and other substances which, given alone, rouse the hibernating animal and restore its body temperature to summer level. Furthermore, insulin will induce a condition of hypoglycæmia in normal animals. This fact is made the basis of the provisional pharmacological standardisation of insulin extracts. A unit dose is described as that amount which on subcutaneous injection will reduce the percentage of blood-sugar in a rabbit of 2 kg., which has been starved for sixteen to twenty-four hours, to 0.045 per cent.<sup>71</sup> The latter figure is chosen because the fall of the blood-sugar to that level is marked in rabbits by the appearance of characteristic symptoms which take the form of violent convulsions and which, with intervals of coma, terminate fatally. The extraordinary fact appears established that there is a definite relationship between the amount of insulin and that of sugar catabolised, for the symptoms of an overdose of insulin can immediately be dispelled by the administration of an appropriate dose of sugar. This also applies to the treatment of human cases.

In addition to restoring a normal blood-sugar level in diabetics, insulin tends to restore the respiratory quotient to normal figure, and also to cause the disappearance of the so-called "acetone bodies" from the urine. In experimental animals, it has also been found to re-establish the normal balance between glycogen and fat in the liver and to restore a normal glycogen content of the heart. The clinical use of insulin is described by Banting, Best, Collip, Campbell, and Fletcher,<sup>72</sup> who find that the administration of suitable doses by subcutaneous injection twice daily removes the cardinal symptoms in a few hours, and, enabling a higher calorific intake to be consumed, leads to an increase of weight and marked improvement in the mental and physical condition of the patient. Much work remains to be done before the remedy can be widely employed, and no small part of its future success will probably depend on whether during

<sup>68</sup> Banting, Best, Collip, Macleod, and Noble, *Trans. Roy. Soc. Canada*, 1922, **16**, Sec.

<sup>69</sup> Macleod, *Brit. Med. J.*, 1922, 833.

<sup>70</sup> *Arch. exp. Path. Pharm.*, 1921, **91**, 110; *A.*, i, 195.

<sup>71</sup> *Amer. J. Physiol.*, 1922, **42**, 162.

<sup>72</sup> *Canad. Med. Assoc. J.*, March, 1922.

the period of insulin treatment the pancreas is able gradually to restore its normal function. However this may be, full credit must be given to the Toronto investigators for a very thorough and painstaking piece of research which has yielded results of fundamental importance both in the clinical treatment of diabetes and in the purely scientific study of sugar consumption in the animal body. It is a regrettable fact that already the armchair critics are busy with attempts to belittle this fine work, and many of the letters which have appeared in the medical Press sadly remind one that the conservatism and jealousies which opposed such advances as were instituted by Pasteur and Lister are by no means dead.

### *Calcium Metabolism and Vitamins.*

Although Professor Barger treated this subject in last year's Report, the advances which have been made during the last twelve months, as well as the widespread interest in this subject, lead me to devote attention to it again this year. Whatever may be their views on the ætiology of rickets, practically all authorities acknowledge the beneficial effects of treatment of this disorder with cod-liver oil. On the one hand, the supporters of theories associating rickets with unhygienic environment or bacterial infection attribute the influence of cod-liver oil to its indirect action in increasing the resistant powers of the body (Paton),<sup>73</sup> whilst those who favour the dietetic origin of the disease tend to ascribe its effect to the presence of an anti-rachitic vitamin. As Mellanby showed<sup>74</sup> in his experimental studies of rickets in dogs, the effect of fats in preventing rickets is roughly parallel to their power to promote growth, and accordingly he inclined to the view that the anti-rachitic vitamin is identical with vitamin-A.

The position has, however, been considerably obscured by a mass of published work on the subject which has appeared during the last year. It would be impossible in the space at my disposal to attempt a review of this work in its entirety, but from it three main conclusions may be drawn. The first is the observation, now generally confirmed, that sunlight or exposure to ultra-violet light will prevent or cure rickets in spite of the diet being defective;<sup>75</sup> secondly, it is apparent that not only a deficiency of some factor present in cod-liver and other oils may induce the onset of rickets, but also that this condition may result from a disturbance of the calcium-phosphate balance in the diet even when the hypothetical

<sup>73</sup> *Brit. Med. J.*, 1922, i, 379; *Glasgow Med. J.*, 1922, 97, 129.

<sup>74</sup> Special Report No. 61, Medical Research Council, 1921.

<sup>75</sup> A. F. Hess and L. J. Unger, *J. Amer. Med. Assoc.*, 1921, 77, 39; *Amer. J. Dis. Child.*, 1921, 22, 186; *Proc. Soc. Exper. Biol. Med.*, 1921, 18, 298.

anti-rachitic vitamin is present in what is believed to be a sufficient amount.<sup>76</sup> Finally, McCollum and his co-workers suspect the existence of an anti-rachitic vitamin distinct from the vitamin-A, which they regard as mainly concerned with growth.<sup>77</sup>

Confirmation of the beneficial action of ultra-violet light has been obtained by most workers, and a particularly interesting investigation which covers this point is reported in a communication by H. Chick, E. L. Dalyell, M. Hume, H. M. M. Mackay, H. H. Smith, and H. Wimberger,<sup>78</sup> who have for two years been making a close study of deficiency diseases in Austria. With regard to the suggestion of the existence of more than one vitamin in certain fats, one feels that the evidence submitted by McCollum tends to support such a view, but that he has perhaps not yet considered the matter sufficiently from the quantitative point of view. As S. S. Zilva and I. Muira<sup>79</sup> showed, cod-liver oil may contain a concentration of vitamin-A more than 200 times greater than that found in butter, and to our mind some of McCollum's results might be explained on this basis as well as by assuming the existence of two separate factors. This has been also pointed out by Zilva.<sup>80</sup> The apparent difference in the destruction of the two factors reported by E. V. McCollum, N. Simmonds, and J. E. Becker,<sup>81</sup> is; however, rather strong evidence in favour of two separate factors, one of which is concerned in growth and the prevention of keratomalacia and the other playing a rôle in calcium deposition.

The whole subject of rickets is reviewed in an excellent monograph by V. Korenchevsky,<sup>82</sup> which contains a very extensive bibliography. The conclusions he has drawn from this review and from his own careful experimental work give general support to the dietetic theories of the origin of the disease. For the prevention of rickets the following factors may, in his opinion, be taken as most important: adequate amounts in the mother's diet of anti-rachitic factor (? vitamin-A), calcium, and phosphates during pregnancy, and especially during lactation; a similar diet for the infant, and abundant light, fresh air, and exercise. Similar conclusions are also drawn from another quarter by H. C. Mann, who has just published the results of a careful clinical investigation into the

<sup>76</sup> E. V. McCollum, N. Simmonds, P. G. Shipley, and E. A. Park, *J. Biol. Chem.*, 1921, 47, 507; *A.*, 1921, i, 757.

<sup>77</sup> E. V. McCollum, N. Simmonds, J. E. Becker, and P. G. Shipley, *Bull. John Hopkins Hosp.*, 1922, 33, 229; Shipley, Park, McCollum, and Simmonds, *Amer. J. Hyg.*, 1921, 1, 512; *Amer. J. Dis. Child.*, 1922, 23, 91.

<sup>78</sup> *Lancet*, 1922, ii, 7.

<sup>79</sup> *Ibid.*, 1921, i, 323.

<sup>80</sup> *Ibid.*, 1922, i, 1244.

<sup>81</sup> *J. Biol. Chem.*, 1922, 53, 292.

<sup>82</sup> Special Report No. 71, Medical Research Council, 1922.



relative importance of environment and diet as factors in the causation of rickets in London children.<sup>83</sup> In view of the discovery of the action of light in preventing and curing rickets, it would appear that convergence of opinion between the two extreme schools of thought will shortly take place. In any case, modern researches leave no excuse for the continuation of the destructive effects of this terrible disease. As has been stated above, there is already general agreement on the beneficial effects of the administration of cod-liver oil in rickets, so that considerable interest attaches to the efforts to isolate the active substance it contains. The older theories attributed the almost specific action of cod-liver oil to various causes. By some it was held that the minute trace of iodine found in the oil is the active constituent, whilst others believed the therapeutic value to be dependent on the small amounts of nitrogen bases frequently present. A third theory which held ground for a long time regarded the peculiar nature of the unsaturated fatty acids as being responsible for the ease with which the oil can be absorbed and utilised by an ill-nourished system. All these theories are now untenable, since it has been shown that the active substance can be transferred almost without loss to the unsaponifiable fraction of the oil, if precautions are taken to prevent oxidation.<sup>84, 85, 86</sup> This fraction contains no detectable trace of nitrogen or iodine and is of course entirely free from fatty acids.<sup>87</sup>

That the anti-rachitic vitamin and vitamin-A are probably of the same type, if McCollum should be correct in thinking that they are not the same substance, is indicated by the observations of T. F. Zucker, A. M. Pappenheimer, and M. Barnett<sup>88</sup> and of T. F. Zucker and M. B. Gutman.<sup>89</sup> Attempts to fractionate the unsaponifiable material from cod-liver oil by J. C. Drummond and K. H. Coward have as yet yielded no positive information regarding the nature of the vitamin.<sup>87</sup> The origin of the vitamin in cod-liver oil and other fish oils has been studied by J. C. Drummond and S. S. Zilva,<sup>90</sup> who drew the conclusion that the primary source is represented by the marine plant life, chiefly unicellular. The actual synthesis of the vitamin by a typical marine diatom, *Nitzschia closterium*, growing in pure culture in an inorganic medium, was demonstrated by H. L. Jameson, J. C. Drummond, and K. H. Coward,<sup>91</sup> whilst the presence of the growth-promoting factor in

<sup>83</sup> Special Report No. 68, Medical Research Council, 1922.

<sup>84</sup> McCollum and M. Davis, *J. Biol. Chem.*, 1914, **19**, 245.

<sup>85</sup> Steenbock and Boutwell, *ibid.*, 1920, **42**, 131.

<sup>86</sup> K. H. Coward and J. C. Drummond, *Biochem. J.*, 1921, **15**, 530.

<sup>87</sup> J. C. Drummond and K. H. Coward, *J. Soc. Chem. Ind.*, 1922, **41**, 561 R.

<sup>88</sup> *Proc. Soc. Exp. Biol. Med.*, 1922, **19**, 167.

<sup>89</sup> *Ibid.*, 1922, **19**, 167.

<sup>90</sup> *Biochem. J.*, 1922, **16**, 518.

<sup>91</sup> *Ibid.*, 1922, **16**, 518.

such organisms has also been recorded by J. Hjort.<sup>92</sup> An exhaustive study of the modern methods of the preparation of cod-liver oil satisfied J. C. Drummond and S. S. Zilva that little appreciable loss of vitamin-*A* occurs, unless attempts are made to bleach oils of inferior quality by methods involving oxidation.<sup>93</sup> These subjects are also arousing considerable interest in agricultural circles.

E. B. Hart, J. G. Halpin, and H. Steenbock<sup>94</sup> have examined the causes of weakness of the legs in chicken and conclude from their investigations that a factor of primary importance in avoiding this trouble is an adequate supply of the vitamins present in cod-liver oil. R. H. A. Plimmer and J. L. Rosedale,<sup>95</sup> while agreeing that the administration of cod-liver oil is of great value to chicken that are being reared on the intensive system, are inclined to attribute the characteristic tendency to weakness of the legs in such birds to an insufficient supply of vitamin-*B*.

The assimilation of calcium by milking cows has been carefully studied by a group of investigators at the University of Wisconsin, and their results have considerable practical importance. E. B. Hart, H. Steenbock, C. A. Hoppert, and G. C. Humphrey<sup>96</sup> have found it possible to maintain milking cows in calcium and phosphorus equilibrium when on a ration of alfalfa (lucerne) hay and cereal products, provided that the hay had been cured in a manner which prevented undue exposure to air or sunlight. When the hay had not been prepared with these precautions,<sup>97</sup> negative calcium balances tended to prevail. The difference in the effect of the two types of hay is attributed to a difference in the degree of destruction of a vitamin which assists calcium assimilation during the curing process. On green alfalfa, calcium retention was more marked than when the hays were used.<sup>98</sup>

### *Lipoids.*

The researches of Levene and his colleagues on lecithins continue to clear up various points concerning the structure of these substances. P. A. Levene and T. Ingvaldsen,<sup>99</sup> and P. A. Levene and H. S. Simms<sup>1</sup> have shown by their studies of liver lecithins that several, possibly four, such compounds exist. Later investigations

<sup>92</sup> *Proc. Roy. Soc.*, 1922, [*B*], **93**, 440.

<sup>93</sup> *J. Soc. Chem. Ind.*, 1922, **41**, 280r.

<sup>94</sup> *J. Biol. Chem.*, 1922, **52**, 379.

<sup>95</sup> *Biochem. J.*, 1922, **16**, 11.

<sup>96</sup> *J. Biol. Chem.*, 1922, **53**, 21.

<sup>97</sup> *Ibid.*, 1922, **54**, 75.

<sup>98</sup> *Ibid.*, 1922, **53**, 21.

<sup>99</sup> *Ibid.*, 1920, **43**, 359; *A.*, 1920, **i**, 788.

<sup>1</sup> *Ibid.*, 1921, **48**, 185; *A.*, 1921, **i**, 842.

have been concerned with the nature of the fatty acids present in egg-lecithin,<sup>2</sup> brain-lecithin,<sup>3</sup> and kephalin.<sup>4</sup> Comparing the mixed lecithins of liver and those of the egg-yolk, the main difference is seen to lie in the much larger proportion of highly unsaturated fatty acids present in the former substances. The possibility has not yet been adequately considered that the variety of lecithins and the highly unsaturated nature of the fatty acids they contain are due to the part which lecithin probably takes in the transport and intermediate metabolism of fats. Brain lecithin and kephalin were found to contain oleic acid as well as acids in which more than one double bond is present. Of the latter acids, arachidonic acid was detected in the form of its octabromo-derivative or by reduction to arachidic acid. Resolution of Linnert's "sahidin" into several fractions, of which one was lecithin, by S. Fränkel and A. Kass<sup>6</sup> has further simplified the list of lipoids, but in another paper the same authors have made up for the loss by describing a new phosphosulphatide from brain.<sup>7</sup>

The substance "tethelin," isolated from the anterior lobe of the pituitary gland, by T. B. Robertson,<sup>8</sup> and believed by him to be the growth-promoting principle of that tissue, has been examined by J. C. Drummond and R. K. Cannan,<sup>9</sup> who conclude that the product is an impure mixture of lipoid substances. They were also unable to confirm that tethelin, or indeed the anterior lobe of the pituitary gland itself, has any effect on the growth of mice when administered by the mouth.

J. C. DRUMMOND.

<sup>2</sup> P. A. Levene and I. P. Rolf, *J. Biol. Chem.*, 1922, **51**, 507; *A.*, i, 621.

<sup>3</sup> *Idem, ibid.*, 1922, **54**, 99; *A.*, 1923, i, 11.

<sup>4</sup> *Idem, ibid.*, 91; *A.*, 1923, i, 11.

<sup>5</sup> *Biochem. Z.*, 1910, **24**, 268.

<sup>6</sup> *Ibid.*, 1921, **124**, 216.

<sup>7</sup> *Ibid.*, 206.

<sup>8</sup> *J. Biol. Chem.*, 1916, **24**, 397; *A.*, 1916, i, 350.

<sup>9</sup> *Biochem. J.*, 1922, **16**, 53; *A.*, i, 491.

## AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

WITH one or two possible exceptions, the year 1922 has not been marked by any really outstanding discoveries in the domain of agricultural and plant chemistry. There has, however, been steady progress along the lines already developed; the results of the work of recent years are being sorted out and viewed in proper perspective; many conflicting views and contradictory findings are being reconciled by the increasing realisation of the complexity of the problems involved; thus the ground is being cleared and, one hopes, suitable jumping-off places are being made in preparation for further advances into the unknown country beyond the present frontiers of our knowledge.

In the present Report the results which have been published in the past year will be utilised in an attempt to indicate the relations of the various parts of this branch of chemistry to one another. This can be done most easily and logically by taking the living plant as the point about which all our problems centre, and considering these problems mainly in their bearings on the plant. The normal development of the living plant depends on an adequate supply of the raw materials from which it builds up its tissues, and on the maintenance of conditions favourable to the processes whereby it effects that synthesis. Of these raw materials all save carbon dioxide, and in certain cases nitrogen, are supplied by the soil, which is therefore considered first under the proposed method of treatment of the subject. The conditions obtaining in the soil are then considered in their relation to the growth of the plant, after which the processes whereby the plant constituents are built up from the raw materials obtained from the soil and from the air are discussed. The chemistry of plant products calls for notice in this Report only in its bearings on the mechanism of the vital processes of the plant and on the characterisation of different species by their constituents. The chemistry of the vegetable micro-organisms forms a distinct branch of the subject, except as regards the micro-organisms of the soil, and is dealt with, so far as space allows, in a separate final section of this Report.

Fertilisers, and the more technical aspects of soil work, including soil analysis, are only dealt with incidentally in this Report. These

aspects of the subject are discussed in the Report to the Society of Chemical Industry on "Soils and Fertilisers."

### *The Soil.*

From the point of view of plant nutrition, the most important of the constituents of the soil system is the liquid phase, the so-called "soil solution," the medium from which the roots absorb moisture and nutrient substances. The concentration and composition of this solution are dependent, on the one hand, on the moisture relationships of the soil, and on the other on the nature of the mineral and organic soil constituents, which are subject to attack by purely chemical and by biological agencies. According to modern conceptions, the particles constituting the mineral framework of the soil are coated with a colloidal layer composed in part of the products of weathering of minerals, and in part of the degradation products of organic residues. This colloidal layer exerts a profound influence on the physical, chemical, and biological properties of the soil.

### *The Soil Colloids.*

*The organic colloidal matter* of the soil is conveniently described as humic matter, although the terms "humus" and "humic acid" now have a more precise significance to the soil chemist: the former term refers to that part of the soil organic matter that is soluble in alkali and precipitated by acids, whilst "humic acid," strictly speaking, consists of that part of the humus that is insoluble in alcohol.

There is considerable controversy in Germany as to the mode of origin and the chemical nature of humic acid, although the question there at issue is the relation of this material to coal formation. Eller and Marcusson<sup>1</sup> have advanced rival theories according to which humic acid is derived from phenolic substances and from furan derivatives, respectively. Marcusson<sup>2</sup> maintains that the humic acids obtained from brown coal contain condensed furan and benzene rings, and that they stand in close relationship to, if they are not identical with, the synthetic acids prepared from sugars. He is supported by Jonas<sup>3</sup> in asserting that Eller's products do not resemble the naturally occurring humic acids, but Eller<sup>4</sup> maintains his position. Schrader has studied the production of humic acid from lignin by alkaline oxidation.<sup>5</sup> The uncertainty of the whole position is really due to the lack of characterisation of

<sup>1</sup> *Ann. Reports*, 1921, 18, 194.

<sup>2</sup> J. Marcusson, *Z. angew. Chem.*, 1922, 35, 165; *A.*, i, 436.

<sup>3</sup> K. J. Jonas, *Brennstoff Chem.*, 1922, 3, 52; *A.*, i, 326.

<sup>4</sup> W. Eller, *ibid.*, 49, 55; *A.*, i, 326.

<sup>5</sup> H. Schrader, *ibid.*, ii, 161; *A.*, i, 637.

humic acid. The grounds on which the various artificial products are stated to be identical with the natural material are usually far from convincing. Further work on the lines of that of Odén<sup>6</sup> on the humic acid of peat is needed; the problem is at present being studied on these lines in the Rothamsted laboratories. The so-called "ulmin" which forms a principal constituent of dopplerite, a gelatinous deposit found in peat bogs, is probably closely related in nature and in mode of formation to the humic acid of the soil. A suggestive investigation of this material has been carried out in this country.<sup>7</sup>

Whatever may be the mechanism of humification, the resulting product is of great importance in the soil. Its action, which consists partly in modifying the moisture relationships and other physical properties of the soil, has been discussed by the reporter.<sup>8</sup>

The *inorganic colloidal matter* of the soil, variously known as the "clay" (in this country), the "ultraclay" (in the United States), or the "colloidal clay" (in Germany), consists of the very fine mineral particles of the soil, and of the products of weathering of the soil minerals. From the fact that the smallest clay particle that could be observed by microscopic methods had a diameter of about 0.0001 mm., Whitney<sup>9</sup> has advanced a hypothesis in which the non-observance of particles smaller than this is assumed to be due to the fact that particles of this size contain so few molecules that they are disintegrated by the bombardment of water molecules, leaving the oxides of silicon, aluminium, and iron in colloidal form. It must, however, be pointed out that particles of diameter less than 0.0001 mm. are beyond the resolving power of the microscope, so that their non-observance is no evidence that they do not exist. Gordon<sup>10</sup> disagrees with Whitney's theory, and prefers to regard the process as based on chemical reactions of hydrolysis, etc. To the writer, this discussion seems to be rather beside the mark; if the nature of the products of weathering of soil minerals, and the effect of conditions on the process, can be elucidated, it matters little whether they are produced by bombardment with water molecules, or by hydrolysis, if indeed these do not both mean practically the same thing.

The effect, on the decomposition of minerals, of micro-organisms such as diatoms<sup>11</sup> or bacteria<sup>12</sup> has been investigated.

<sup>6</sup> For example, S. Odén, *Trans. Faraday Soc.*, 1922, **17**, 288.

<sup>7</sup> F. V. Tideswell and R. V. Wheeler, *T.*, 1922, **121**, 2345.

<sup>8</sup> H. J. Page, *Trans. Faraday Soc.*, 1922, **17**, 272.

<sup>9</sup> M. Whitney, *Science*, 1921, **54**, 653; *A.*, i, 708.

<sup>10</sup> N. E. Gordon, *ibid.*, 1922, **55**, 676; *A.*, i, 1227.

<sup>11</sup> W. J. Vernadsky, *Compt. rend.*, 1922, **175**, 450; *A.*, i, 1096.

<sup>12</sup> D. Wright, *Calif. Univ. Pubs. Agric. Sci.*, 1922, **4**, 245.

It has been shown<sup>13</sup> that the values of such physical constants of a soil as density, pore space, water-absorbing power, swelling on moistening, are directly related to the amount of clay or organic matter in the soil.

*The flocculation of soils*, which has such an important bearing on the moisture relationships, and on tilth, is of course a function of the colloidal matter in the soil. Comber's hypothesis with reference to the flocculation of soils by lime<sup>14</sup> has been developed and strengthened by further work<sup>15</sup>; it seems reasonably certain that the "abnormal" flocculation of clay by calcium salts in the presence of alkali is due to the emulsoid siliceous gel coating around the particles, which masks to a greater or less degree the suspensoid properties of the mineral core. The same hypothesis has been used to explain the difference between what are known in the ceramic industry as "fat" and "lean" clays.<sup>16</sup> A comprehensive study of the flocculation of clay and peat by calcium salts in alkaline solution has also been carried out by Mattson.<sup>17</sup> Clay suspensions, if left undisturbed, frequently show a curious layer formation. This phenomenon has been investigated,<sup>18</sup> and it is stated that in any one layer the particles are of uniform size, and that the space between the layers contains particles uniformly dispersed. From the rate of rise or fall of the layers the size of the particles may be calculated by means of Stokes's law. Clays of different origin and different reaction have been found to have the same isoelectric point.<sup>19</sup> Flocculation has been used as the basis of a method for the determination of colloidal clay in soils<sup>20</sup> and it is claimed that the method is more trustworthy than that based on hygroscopicity measurements.

*Absorption and basic exchange*, between the soil colloids and the constituents of the soil solution, have an important bearing on the composition and concentration of the latter. Many of the shortcomings of present methods of soil analysis may be ascribed to a lack of sufficient discrimination between that part of the bases of the soil which is absorbed, and therefore capable of liberation by basic exchange, and that part which is actually insoluble, but

<sup>13</sup> B. A. Keen and H. Raczkowski, *J. Agric. Sci.*, 1921, **11**, 441.

<sup>14</sup> *Ann. Reports*, 1920, **17**, 186.

<sup>15</sup> N. M. Comber, *J. Agri. Sci.*, 1921, **11**, 450; *A.*, i, 212; *ibid.*, 1922, **12**, 372; see also *Trans. Faraday Soc.*, 1922, **17**, 349.

<sup>16</sup> N. M. Comber, *J. Soc. Chem. Ind.*, 1922, **41**, 77π.

<sup>17</sup> S. E. Mattson, *Koll. Chem. Beihefte*, 1922, **14**, 227; *A.*, i, 800.

<sup>18</sup> E. Ungerer, *ibid.*, 1921, **14**, 63; *A.*, ii, 96.

<sup>19</sup> O. Arrhenius, *J. Amer. Chem. Soc.*, 1922, **44**, 521; *A.*, i, 707.

<sup>20</sup> R. Sokol, *Internat. Mitt. Bodenkunde*, 1921, **11**, 184.

capable of solution by acids. Hissink<sup>21</sup> has carried out a suggestive investigation on this point, which merits detailed perusal. The present state of our knowledge of absorption and basic exchange in soils has been reviewed by Fisher<sup>22</sup> and by von Nostitz,<sup>23</sup> who has demonstrated how the whole of the readily available potash in a soil may be removed by basic exchange with ammonium nitrate, followed by leaching, so that plants grown on soil so treated show all the symptoms of potash-starvation. The influence of soil colloids and of hydrogen-ion concentration on the availability of calcium, potassium, and phosphates<sup>24</sup> and of ammonium salts<sup>25</sup> has also been investigated.

### *Biochemical Changes in the Soil.*

The composition of the soil solution is influenced not only by the chemical processes of weathering and the like, and by physico-chemical phenomena such as absorption and basic exchange, but also to an even greater extent by the biochemical processes brought about by the plentiful and varied soil microflora and microfauna.

*The nitrogen cycle*—the complex series of reactions through which the nitrogen compounds of the soil pass—is perhaps of the greatest importance in this connexion. Nitrogen is added to the soil in the form of artificial fertilisers and of plant and animal residues, and by means of biological fixation, whilst it may be lost by leaching, by evolution of gaseous nitrogen, and by absorption by the growing crop. The level at which the nitrogen content of any soil stands depends on the interaction of these factors, which are variously affected by different conditions.<sup>26</sup>

Nitrogen fixation by free-living bacteria in the soil is a factor as to the quantitative importance of which under field conditions there is still some uncertainty. The influence of salts on the process has been investigated<sup>27</sup>; it was found that nitrogen-fixing bacteria were much more resistant to the toxic action of salts than are ammonifiers and nitrifiers, and that many common soil salts had a stimulating action. Boric acid causes increased fixation by *Azotobacter chroococcum* in the presence of humus, although its

<sup>21</sup> D. J. Hissink, *Internat. Mitt. Bodenkunde*, 1922, **12**, 81.

<sup>22</sup> E. A. Fisher, *Trans. Faraday Soc.*, 1922, **17**, 305.

<sup>23</sup> A. von Nostitz, *Mitt. deut. landw. Ges.*, 1921, **36**, 608; *A.*, i, 511; *J. Landw.*, 1922, **70**, 45.

<sup>24</sup> N. E. Gordon and E. B. Starkey, *Soil Sci.*, 1922, **14**, 1; *A.*, i, 1104.

<sup>25</sup> B. Aarnio, *Z. Pflanz. Düng.*, 1922, [*A.*], **1**, 320; *A.*, i, 1227.

<sup>26</sup> For a discussion of this problem see F. E. Bear, *J. Amer. Soc. Agron.*, 1922, **14**, 136.

<sup>27</sup> J. E. Greaves, E. G. Carter, and Y. Lund, *Soil Sci.*, 1922, **13**, 481; *A.*, i, 976.



action in absence of the latter is inappreciable. The same is true of its toxic effect in higher concentrations.<sup>28</sup> A new nitrogen-fixing bacillus has been described.<sup>29</sup> The functions of the unicellular green algae which are present in most soils are not yet known. According to Wann,<sup>30</sup> they can assimilate atmospheric nitrogen; this result, if confirmed, might be of considerable importance in relation to the nitrogen economy of the soil; according to work (as yet unpublished) in the Rothamsted laboratories, however, the question cannot yet be taken as settled.

A moment's reflection will show that in the process of ammonification, whereby the nitrogen of the complex organic material of plant residues and the like is rendered soluble by the action of soil micro-organisms, the initial stages of the action of these organisms must depend largely and probably exclusively on extracellular enzymes, since the complex materials are all insoluble or colloidal, and therefore presumably cannot be absorbed as such into those micro-organisms which feed "osmotically." Several of the bacteria which are most commonly found in the soil have been shown<sup>31</sup> to produce extracellular proteases which were active within a range of hydrogen-ion concentration of  $p_H$  4—9, with an optimum zone of 6 to 7, a zone closely corresponding with the average hydrogen-ion concentration of a fertile soil. Moulds may also be active ammonifying agents; the production of ammonia from protein by the action of *Aspergillus niger* has been investigated.<sup>32</sup> The biological degradation of organic nitrogen compounds in humus forest soils has also been investigated.<sup>33</sup>

Nitrification—the final stage in the chain of reactions whereby organic nitrogen in the soil is rendered available to the plant—is a process requiring an ample supply of air. The physical condition of the soil thus has a direct effect on nitrate formation; this aspect of the subject has received further study.<sup>34</sup> The kinetics of nitrification have also been investigated;<sup>35</sup> the reaction as a whole is found to be an autocatalytic unimolecular reaction, increase in nitric acid being in accordance with the equation:

$$\log x - \log(A - x) = K(t - t').$$

The proportions of the total nitrogen of a soil which are present

<sup>28</sup> J. Voicu, *Compt. rend.*, 1922, **175**, 317.

<sup>29</sup> G. Truffaut and N. Bezssonoff, *ibid.*, 544.

<sup>30</sup> F. B. Wann, *Amer. J. Bot.*, 1922, **8**, 1.

<sup>31</sup> K. G. Dernby, *Biochem. Z.*, 1921, **126**, 105; *A.*, i, 405.

<sup>32</sup> V. S. Butkevitch, *ibid.*, 1922, **129**, 445; *A.*, i, 707; see also *A.*, i, 973.

<sup>33</sup> H. Suchting, *Z. Pflanz. Düng.*, 1922, **1**, 113.

<sup>34</sup> P. H. Carpenter and A. K. Bose, *Ind. Tea Assoc., Sc. Dept. Quart. J.*, 1921, 103; see also T. L. Lyon, *J. Amer. Soc. Agron.*, 1922, **14**, 97.

<sup>35</sup> K. Miyake and S. Soma, *J. Biochem. (Japan)*, 1922, **1**, 123; *A.*, i, 1096.

at any time in the form of soluble nitrate and of insoluble organic compounds depend on the interaction of the various groups of micro-organisms, and on their conditions. Thus it is known that in the presence of an abundance of a non-nitrogenous source of energy, such as carbohydrate, much of the soluble nitrogen in the soil is reassimilated by the soil organisms and thus locked up for a time in a form in which it is not available to the plant. The effect of a straw mulch in depressing the nitrate content of the soil has been investigated.<sup>36</sup> This depression is greatest when the soil is at its wettest after rain; and it seems probable that this result is to be explained by the washing down into the soil of soluble decomposition products of the straw, which would then exert the action above mentioned.<sup>37</sup>

The sulphur cycle has received a considerable amount of attention of recent years. The reduction of sulphates to sulphides under anaërobic conditions, such as obtain in deep subsoils, has been found to occur in depths from 10 metres to 34.5 metres in the Amsterdam district.<sup>38</sup> The organism operative in this process is *Microspira desulphuricans*. Sulphides are similarly found in the lower layers of peat soils.<sup>39</sup> Under aërobic conditions, on the other hand, sulphate formation occurs. Demolon<sup>40</sup> has studied the sulphur-oxidising power of soils and concludes that the ammonifying organisms are apparently responsible, and that the property is not bacteriologically specific. Sulphur-oxidation has, however, received most attention at the New Jersey Experiment Station, by J. G. Lipman and his co-workers. Two specific organisms, *Thiobacillus thio-oxidans* and *Thiobacillus B.*, have been isolated;<sup>41</sup> the former, which acts best in acid media, is not commonly found in cultivated soils, except after treatment with sulphur; the latter, which acts in alkaline solution, appears to be closely related to Beijerinck's *Thiobacillus thioparus*, and is commonly present in cultivated soils in America, especially "black alkali" soils. *Thiobacillus thio-oxidans* is an extraordinary organism; its optimum growth occurs at a hydrogen-ion concentration of  $p_H$  2.8—2.0, and it can exist in a medium of  $p_H$  0.58.<sup>42</sup> It is auto-

<sup>36</sup> W. A. Albrecht, *Soil Sci.*, 1922, **14**, 299.

<sup>37</sup> See also J. A. Bizzell, *J. Amer. Soc. Agron.*, 1922, **14**, 320.

<sup>38</sup> C. A. H. von Wolzogen Kühr, *Proc. K. Acad. Wetensch. Amsterdam*, 1922, **25**, 188; *A.*, i, 1228.

<sup>39</sup> C. O. Rost, *Soil Sci.*, 1922, **14**, 167.

<sup>40</sup> A. Demolon, *Compt. rend.*, 1921, **173**, 1408; *A.*, i, 312.

<sup>41</sup> S. A. Waksman, *J. Bact.*, 1922, **7**, 231, 605, 609; *Soil Sci.*, 1922, **13**, 329; *A.*, i, 706; S. A. Waksman and J. S. Joffe, *J. Bact.*, 1922, **7**, 239; J. S. Joffe, *Soil Sci.*, 1922, **13**, 161.

<sup>42</sup> J. G. Lipman, S. A. Waksman, and J. S. Joffe, *Soil Sci.*, 1921, **12**, 475; *A.*, i, 303.

trophic, utilising sulphur as a source of energy, and assimilating carbon dioxide. It has also been found that certain bacteria can oxidise zinc blende to zinc sulphate.<sup>43</sup> Lantzsck concludes, from an investigation into the various phases of the sulphur cycle, that "the sulphur cycle in soil does not justify the assumption that free sulphuric acid is produced (directly or via hydrogen sulphide) and exerts a solvent action. An increase of soil acidity is obtained only with heavy dressings of sulphur."<sup>44</sup> The bearings of sulphur-oxidation on the soil reaction and on crop production are discussed later in this Report.

Lantzsck<sup>45</sup> also suggests the possibility of a direct connexion between nitrification and the solubility of the phosphates of the soil, inasmuch as it is stated that the seasonal maxima of nitrate content of the soil coincide with maxima for the phosphate content of the soil solution.

#### *Soil Moisture and the Soil Solution.*

The moisture relationships of the soil, which are so dependent on the amount of colloidal matter present, themselves have a direct bearing on the strength of the soil solution, inasmuch as the extent to which the latter may be subject to dilution or concentration varies with the moisture-holding capacity of, and rate of evaporation of water from, the soil. It has been found that the absorption of water by the colloidal matter extracted from a number of widely different American soils was relatively constant.<sup>46</sup> Odén has published a suggestive note on the hygroscopicity of clay.<sup>47</sup> The rate of evaporation of water from a soil receiving farmyard manure every year, and therefore relatively rich in colloidal organic matter, is less than that from unmanured soil or from soil receiving only artificial fertilisers.<sup>48</sup> The evaporation of water from soil in the field has been investigated by Helbig and Rössler.<sup>49</sup> Evaporation of water from the soil tends to cause an accumulation of soluble salts in the surface layers of the soil. This takes place, as would be expected, during the summer months, especially in a dry summer, and is most pronounced in the top quarter of an inch of the soil.<sup>50</sup> In this investigation the concentration of soluble salts was deter-

<sup>43</sup> A. Helbronner and W. Rudolfs, *Compt. rend.*, 1922, **174**, 1378; *A.*, i, 706.

<sup>44</sup> K. Lantzsck, *Internat. Mitt. Bodenkunde*, 1922, **12**, 22.

<sup>45</sup> K. Lantzsck, *loc. cit.*

<sup>46</sup> W. O. Robinson, *J. Physical Chem.*, 1922, **26**, 647; *A.*, i, 1228; see also R. O. E. Davis, *J. Amer. Soc. Agron.*, 1922, **14**, 293.

<sup>47</sup> S. Odén, *Trans. Faraday Soc.*, 1922, **17**, 244.

<sup>48</sup> B. A. Keen, *J. Agric. Sci.*, 1921, **11**, 433.

<sup>49</sup> M. Helbig and O. Rössler, *Z. Pflanz. Dung.*, 1922, **1**, 95.

<sup>50</sup> C. E. Millar, *Soil Sci.*, 1922, **13**, 433.

mined by the freezing-point method, which has been extensively studied by Bouyoucos. This worker concluded<sup>51</sup> from freezing-point and dilatometer measurements that a portion of the soil moisture was "unfree," and inactive as a solvent. Parker now presents evidence<sup>52</sup> that Bouyoucos's assumptions are not well founded, and that soils do not contain a considerable percentage of water which does not act as a solvent. Although the old classification of soil moisture into hygroscopic, capillary, and gravitational water has certain objections, it seems to be the best yet offered. Keen<sup>53</sup> has published a useful general discussion of modern views on the moisture relationships of the soil.

As an alternative to the examination of the soil solution *in situ*, several methods have been devised for isolating it from the soil. These methods fall into several categories, one of which is the application of very high pressures to the moist soil. This method was used in California by C. B. Lipman, and it has now been developed in the same laboratory by Burgess,<sup>54</sup> who by the application of pressures up to 16,000 lb. per square inch has succeeded in expressing from soils at a moisture content of 50 per cent. of their moisture-holding capacity, between 45 and 60 per cent. of their total moisture. By an examination of the composition of the liquid so expressed, and comparison with a 1 : 5 water extract, it is concluded that the liquid obtained by the direct pressure method does represent the true soil solution, and further, that the balance of evidence is against the existence of "unfree" water, thus confirming Parker's conclusions.<sup>55</sup>

In the reporter's opinion, there is still some reason to doubt whether any of the methods for isolating the soil solution are really capable of doing so, at any rate for heavy soils, in which the amount of colloidal matter is high. These methods are usually most successful with coarse soils, in which it is not difficult to suppose that a large part of the soil solution may be regarded as existing as a free water film on the surface of the comparatively bare mineral grains. For heavy soils much greater difficulties are encountered, as noticed by Burgess<sup>56</sup> with the Parker displacement method, and this is confirmed by experience of the same method in the Rothamsted laboratories. In such soils it must be supposed that the soil solution is to a large extent imbibed in the capillary channels of the compound particles, and in the hydrophilous gel

<sup>51</sup> *Ann. Reports*, 1921, 18, 200.

<sup>52</sup> F. W. Parker, *Soil Sci.*, 1922, 13, 43; *A.*, i, 116.

<sup>53</sup> B. A. Keen, *Trans. Faraday Soc.*, 1922, 17, 228. For "Wilting point" see also W. L. Power, *Soil Sci.*, 1922, 14, 159.

<sup>54</sup> P. S. Burgess, *Soil Sci.*, 1922, 14, 191.

<sup>55</sup> F. W. Parker, *loc. cit.*

<sup>56</sup> P. S. Burgess, *loc. cit.*

coating of the particles; it will therefore be more difficult to remove than that in a coarse soil containing little colloidal matter, and in a displacement method the possibility of dilution by the displacing liquid will be considerable. The degree of hydration of the gel coating on the particle is doubtless much greater on the outside than towards the surface of the mineral "core." If this is so, it follows that by any method in which an attempt is made to remove the soil solution from the soil, a part of this solution will be removed with greater ease than the rest; if at the same time it is assumed—and there appears to be some grounds for the assumption—that there is a concentration gradient in the soil solution as between the outside and the inner layers of the gel coating of the particles, then it would follow that the first portions of the expressed soil solution would have a different concentration from that of the portions removed later. This is not found for relatively coarse soils, but there is some indication of it in Burgess's results<sup>56</sup> for soils containing a fair amount of clay. The concentration of the true soil solution could then only be expressed as a mean value, represented possibly by that of a portion of the solution collected when about half of the original soil moisture had been isolated from the soil.

*The reaction of the soil solution* continues to provoke a bigger volume of work than practically any other soil problem. Much confusion has resulted in this field from the fact that "soil acidity" is a complex phenomenon, in the development of which several distinct factors are involved; these have not always been clearly distinguished. Lemmerman and Fresenius<sup>57</sup> emphasise this point, and distinguish three types of soil acidity: (1) actual acidity of the soil solution, due to the presence of acids; (2) latent acidity, developed in the presence of neutral salts, owing to the liberation, by basic exchange, of readily hydrolysed iron and aluminium salts; (3) latent acidity, developed in the presence of salts of weak acids with strong bases, the base being absorbed by the soil colloids and the acid left. The measurement of the hydrogen-ion concentration of the soil solution<sup>58</sup> does not necessarily give any indication of the amount of base required to bring about neutrality; this is determined partly by the buffer action of some of the soil constituents,<sup>59</sup> and partly by the fact that some of the base is precipi-

<sup>56</sup> P. S. Burgess, *loc. cit.*

<sup>57</sup> O. Lemmermann and L. Fresenius, *Z. Pflanz. Düng.*, 1922, [A], 1, 12; A., i, 510.

<sup>58</sup> See, for example, D. J. Healy and P. E. Kanaker, *Soil Sci.*, 1922, 13, 323; A., i, 519.

<sup>59</sup> E. A. Fisher, *Nature*, 1921, 108, 306; A., i, 510; H. W. Johnson, *Soil Sci.*, 1922, 13, 7; A., i, 708.

ated or absorbed by the soil colloids. Calcium hydroxide and bicarbonate are involved in this latter effect to different extents; this helps to explain the different "lime-requirement" values given by the use of these two reagents.<sup>60</sup> The titration curve obtained by measuring the rate of change of hydrogen-ion concentration on the gradual addition of acids and alkalis gives valuable information as to the magnitude of the buffer effects in a soil, which will determine to what extent the latent acidity of the types specified under (2) and (3) above can produce harmful effects in the soil.<sup>61</sup> A well-buffered soil is more productive than a badly buffered one; clay soils are better buffered than sandy soils.<sup>62</sup> The relation of the soluble iron or aluminium of the soil to soil acidity forms the basis of Comber's qualitative test,<sup>63</sup> now described in a modified form; <sup>64</sup> a "lime-requirement" method based on this test has been described.<sup>65</sup> It is usually supposed that acidity may be caused by the presence of aluminium salts owing to their ready hydrolysis. It is now suggested, however, that the presence of soluble aluminium salts in soils is the result rather than the cause of soil acidity.<sup>66</sup> It seems likely that the first explanation may be correct in some cases, as in case (2) above, and the second in other cases, as, for instance, when mineral acid is produced in the soil by the use of "physiologically acid" fertilisers like sulphate of ammonia, or by the oxidation of sulphur. Crowther <sup>67</sup> has published a review of the physico-chemical aspects of soil acidity.

The use of the bacterial oxidation of sulphur as a means of increasing the hydrogen-ion concentration of the soil continues to attract much attention in America. Potato scab disease can be controlled by treating the soil with sulphur inoculated with *Thiobacillus thio-oxidans*, the acidity produced by the oxidation of the sulphur being sufficient to inhibit the growth of *Actinomyces scabies*, the organism responsible for the disease.<sup>68</sup> Similarly, the alkalinity of "black alkali" soil can be reduced by treatment

<sup>60</sup> V. Vincent, *Compt. rend.*, 1922, **175**, 1233.

<sup>61</sup> E. A. Fisher, *loc. cit.*; see also C. H. Spurway, *Michigan Agric. Exp. Sta., Technical Bull.* No. 57; October, 1922.

<sup>62</sup> O. Arrhenius, *loc. cit.*, and *Soil Sci.*, 1922, **14**, 223.

<sup>63</sup> *Ann. Reports*, 1920, **17**, 178; see also J. Hudig and C. W. G. Hetterschij, *Chem. Weekblad*, 1922, **19**, 366; *A.*, i, 1104.

<sup>64</sup> N. M. Comber, *J. Agric. Sci.*, 1922, **12**, 370.

<sup>65</sup> R. H. Carr, *J. Ind. Eng. Chem.*, 1921, **13**, 931; *A.*, i, 172.

<sup>66</sup> I. A. Denison, *Soil Sci.*, 1922, **13**, 81; *A.*, i, 512.

<sup>67</sup> E. M. Crowther, *Trans. Faraday Soc.*, 1922, **17**, 317.

<sup>68</sup> S. A. Waksman, *Soil Sci.*, 1922, **14**, 61; see also W. H. Martin, *ibid.*, 1921, **11**, 75.

with inoculated sulphur, although it is also necessary to leach out the salts if the full benefit is to be obtained.<sup>69</sup>

*The Effect of Soil Conditions and of Fertilisers on Plant Growth.*

In the first section of this Report, the work of the past year has been considered in relation to the influence of the various soil factors on the soil solution; in this section, the relation of the soil solution to the growth of the plant will be discussed.

*The effect of the concentration of the soil solution* on plant growth is a question which is at present but little understood. The usually accepted view is that the plant root absorbs nutrient ions from the soil solution by osmosis. On this view, there will probably be for any plant a *minimum* concentration for each ion, below which the plant is unable to absorb that ion. The minimum value will vary for different ions and for different plants. The lack of knowledge as to the values of these minima is partly responsible for the difficulty of interpreting the results of soil analysis in terms of soil fertility. Vesterberg<sup>70</sup> has discussed this point, and from an examination of various data he has put forward tentative average values for these minima for nitrogen, potash, and phosphate. When the requirements of any plant have been ascertained, it will then be necessary to find, for any given soil, (1) whether it can give the required concentration in the soil solution and (2) whether it can maintain it. Comber,<sup>71</sup> however, advances an interesting modification of the present osmotic hypothesis of the mechanism of root absorption in the soil. He maintains that the assumption that plants feed in the soil just as they feed in water cultures is unjustified and contrary to the facts. He adduces evidence in favour of the view that colloids can be directly absorbed by the plant, and advances the hypothesis that there is a direct union of the root hair with the particles of the soil; this union is brought about by colloidal mucilaginous matter from the cell wall of the root hair on the one hand, and the hydrophilous gel coating around the soil particle on the other, which intermingle to form one system, thereby enabling the direct absorption of colloids, and permitting the acid juices of the plant cell to attack directly the particles of the soil. The acceptance of this hypothesis would, of course, necessitate a radical reconsideration of our views regarding the relation of the soil solution to the plant.

*The effect of the composition of the soil solution* on plant growth

<sup>69</sup> W. Rudolfs, *Soil Sci.*, 1922, **13**, 215.

<sup>70</sup> K. A. Vesterburg, *Internat. Mitt. Bodenkunde*, 1922, **12**, 11.

<sup>71</sup> N. M. Comber, *J. Agric. Sci.*, 1922, **12**, 363.

may next be considered. Besides the ammonium salts and nitrates produced by biological agencies in the soil, it is concluded from a study of the action of alkaline permanganate that the nitrogen present in the soil as amino-acids, and part of that present as acid amides, are immediately available.<sup>72</sup> It is doubtful, however, whether such substances are normally present in sufficient amount to be of importance.

Some American soils seem to be actually deficient in sulphates, so that they give increased crops by treatment with sulphur.<sup>73</sup> For this treatment to be successful, the dressings must be small, otherwise if the oxidising power of the soil is high and the soil not well buffered, the hydrogen-ion concentration is increased to a point at which the plant suffers.<sup>74</sup>

The utilisation of phosphates varies for different species of plants, and appears to bear a direct relation to the ratio  $\text{CaO} : \text{P}_2\text{O}_5$  in the ash of the plant.<sup>75</sup> Ammonium humate or colloidal humic acid is stated to increase the solubility of mineral phosphates and thus to give rise to increased phosphate assimilation.<sup>76</sup> It is also stated that the same effect is obtained by the active nitrification of urea,<sup>77</sup> thus supporting the suggestion of Lantzsche.<sup>78</sup> It is not practicable to render mineral phosphates more soluble by direct application of sulphur to the soil, since the hydrogen-ion concentration required to effect the transformation ( $p_{\text{H}}$  3.1—2.8) is harmful to plants.<sup>79</sup> In the Rothamsted field experiments, it has long been found that increased yields are obtained on phosphate-deficient soil by the application of sodium silicate, and it is usually supposed that this effect is due to increased assimilation of phosphate in the presence of silica. Lemmermann and Wiessman<sup>80</sup> have obtained similar results in pot experiments using colloidal silica, but they obtained significant increases also in the complete absence of phosphates, from which they conclude that colloidal silica has a

<sup>72</sup> C. S. Robinson, O. B. Winter, and E. J. Millar, *J. Ind. Eng. Chem.*, 1921, 13, 933; *A.*, i, 212.

<sup>73</sup> See, for example, F. C. Reimer and H. V. Tartar, *Oregon Agric. Exp. Sta., Bull.*, 163, 1919; also J. Woodard, *Bot. Gaz.*, 1922, 73, 81.

<sup>74</sup> W. Rudolfs, *Soil Sci.*, 1922, 14, 247; see also J. S. Joffe and H. C. McLean, *ibid.*, 217. For German experience see B. Heinze, *Z. Pflanz. Düng.*, 1922, [4], 1, 154; E. Kruger, *ibid.*, 166; Gerlach, *Mitt. Deut. landw. Ges.*, 1921, 36, 726.

<sup>75</sup> M. von Wrangell, *Landw. Jahrb.*, 1922, 57, 1; *A.*, i, 1098.

<sup>76</sup> K. Mack, *Chem. Ztg.*, 1922, 46, 73.

<sup>77</sup> J. S. Marais, *Soil Sci.*, 1922, 13, 355.

<sup>78</sup> K. Lantzsche, *loc. cit.*

<sup>79</sup> W. Rudolfs, *loc. cit.*

<sup>80</sup> O. Lemmermann and H. Wiessmann, *Z. Pflanz. Düng.*, 1922, [4], 1, 185; *A.*, i, 1103.



direct effect on plant growth, and that it acts in the presence of phosphate deficiency by virtue of an ability partly to replace phosphate in the plant. They do not appear, however, to have determined the amounts of phosphate and silica taken up by the increased crops; this would throw light on the relative importance of the supposed direct action of the silica on the plant and of its possible indirect action in causing increased assimilation of phosphates. Shedd<sup>81</sup> has also obtained increased growth by the application of silica.

One of the effects of potash on the plant is to increase its vigour, and its resistance to disease. This is well instanced by a result reported from Arkansas;<sup>82</sup> on a control plot receiving no potash, 95 per cent. of the cotton plants died from the wilt disease, whereas on the plot receiving kainit not a single plant was affected.

Experiments in Kentucky<sup>83</sup> indicate that some soils may be deficient in calcium, and that by the application of salts of this metal, crop increases may be obtained which are not due merely to decreased hydrogen-ion concentration.

*The effect of the reaction of the soil solution on plant growth* is gradually being elucidated. Sour soils are recognised agriculturally by well-defined symptoms, such as the growth of certain characteristic weeds, the liability of cruciferous crops to "finger and toe" disease, and the failure of most leguminous crops. It does not follow, however, that a soil which is "acid" according to chemical tests is "sour" in the agricultural sense; the hydrogen-ion concentration which is definitely harmful varies greatly for different crops,<sup>84</sup> and under undisturbed natural conditions the character of the flora may be largely influenced by the reaction of the soil solution.<sup>85</sup> Most common crop plants appear to be unaffected by, and even possibly to prefer, a faintly acid medium. Thus it has been shown<sup>86</sup> that although peas, maize, wheat, oats, and carrots all germinated most slowly at hydrogen-ion concentrations of  $p_H$  5—6, root growth after ten days was at a maximum between these values, which are regarded as representing the values for normal growth. There is always a tendency, when a plant is

<sup>81</sup> O. M. Shedd, *Soil Sci.*, 1922, **14**, 233.

<sup>82</sup> L. E. Rast, *J. Amer. Soc. Agron.*, 1922, **14**, 222.

<sup>83</sup> O. M. Shedd, *loc. cit.*, and *Kentucky Agr. Exp. Sta. Bull.*, 236 (1921); A., ii, 527.

<sup>84</sup> See, for example, O. Lemmermann and L. Fresenius, *loc. cit.*

<sup>85</sup> E. J. Salisbury, *Ann. Bot.*, 1922, **36**, 391; A., i, 1104; W. R. G. Atkins, *Nature*, 1921, **108**, 80; A., i, 415; *Sci. Proc. Roy. Dubl. Soc.*, 1922, **16**, 369; A., i, 509; A. P. Kelley, *Soil Sci.*, 1922, **13**, 411; C. Olsen, *Science*, 1921, **54**, 539.

<sup>86</sup> R. M. Hixon, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **4**, No. 91; A., i, 1221; see also O. Arrhenius, *J. Gen. Physiol.*, 1922, **5**, 81; A., i, 1097.

growing in a solution with a hydrogen-ion concentration towards one extreme, for the plant to modify this value towards one lying between  $p_H$  5.0 and 6.8. The cell-sap of many plants is acid,<sup>87</sup> and it has been found that plants may tend to alter the acidity of the soil solution so as to bring it closer to that of their own root sap.<sup>88</sup> On the other hand, the acidity of the plant juices may be directly influenced by that of the soil solution.<sup>89</sup> The harmful effect of sour soils may often be due not so much to the acidity of the soil solution as to the soluble iron and aluminium compounds they contain.<sup>90</sup> Soil acidity may also affect soil fertility indirectly by its deleterious effect on many of the micro-organisms concerned in the nitrogen cycle. Thus nitrification is hindered by acidity: a case is reported where a strong nitrite reaction developed in a soil at  $p_H$  3.9—4.4,<sup>91</sup> whilst in another instance, it was found that those acid soils which responded to lime in the field were the ones in which lime treatment caused a rapid formation of nitrates.<sup>92</sup> Growth of, and nitrogen fixation by, *Azotobacter* are inhibited by acidity higher than  $p_H$  5.9—6.0.<sup>93</sup>

The effect of partial sterilisation of the soil by arsenates and arsenites<sup>94</sup> and by various aromatic substances<sup>95</sup> has been studied.

Russell and Hutchinson's view of the mechanism of partial sterilisation is that the sterilising agent kills off the soil protozoa, which normally limit the numbers of beneficial bacteria in the soil, and thus enables the latter to attain greatly increased numbers and to produce increased quantities of plant nutrients.<sup>96</sup> Much discussion has centred round this hypothesis. From an experiment at Rothamsted in which the numbers of active amœbæ and of bacteria in a field soil were counted daily for 365 days, it has been clearly established that there is a definite inverse relationship

<sup>87</sup> See, for example, W. R. G. Atkins, *Sci. Proc. Roy. Dubl. Soc.*, 1922, **16**, 414; *A.*, i, 411.

<sup>88</sup> J. König, J. Hasenbäumer, and E. Kröger, *Z. Pflanz. Düng.*, 1922, [A], 1, 3; *A.*, i, 510.

<sup>89</sup> F. C. Bauer and A. R. C. Haas, *Soil Sci.*, 1922, **13**, 461; *A.*, i, 975.

<sup>90</sup> S. D. Conner and O. H. Sears, *ibid.*, 23; *A.*, i, 613; N. M. Comber, *Nature*, 1921, **108**, 146; *A.*, i, 416; C. H. Arndt, *Amer. J. Bot.*, 1922, **9**, 47; *A.*, i, 1103.

<sup>91</sup> F. C. Gerretsen, *Arch. Suikerindus. Nederland-Indië*, 1921, **29**, 1397; *Exp. Sta. Rec.*, 1922, **47**, 214.

<sup>92</sup> R. H. Robinson and D. R. Bullis, *Soil Sci.*, 449; *A.*, i, 976.

<sup>93</sup> P. L. Gainey and H. W. Batchelor, *Science*, 1922, **56**, 49; *A.*, i, 1096.

<sup>94</sup> G. Rivière and G. Pichard, *Compt. rend.*, 1922, **174**, 493; R. Ciferri, *Coltivatore*, 1922, Nos. 32—34.

<sup>95</sup> T. Parker, A. W. Long, and J. S. Mitchell, *Bull. Bur. Bio-Tech.*, 1922, No. 5, 134.

<sup>96</sup> E. J. Russell and H. B. Hutchinson, *J. Agric. Sci.*, 1909, **3**, 111; 1913, **5**, 152.

between the numbers of these two types of organisms: when the numbers of active amoebæ are high, those of the bacteria are low, and vice versa;<sup>97</sup> these results lend very considerable support to Russell and Hutchinson's hypothesis, and show that however many factors there may be which play a part in partial sterilisation, the elimination of the protozoa by the process is by no means the least important.

*The relation of crop yield to amount of fertiliser used*, and Mitscherlich's application thereto of the "law of minimum" still provoke controversy in Germany.<sup>98</sup> The question is of considerable practical importance, particularly at a time of agricultural depression such as the present. There are now some indications<sup>99</sup> that at first increasingly large crop increments may be obtained by successive equal increases in the amount of fertiliser used, and that only with relatively large dressings does the "law of diminishing returns" come into play; the curve for the relation of yield to amount of fertiliser appears to be sigmoid rather than logarithmic in form.

### *The Chemistry of Plant Processes.*

Having discussed the soil and the influence on plant growth of soil factors, including the nutrient materials derived from the soil, it remains to deal with the processes going on within the plant itself.

#### *Carbon Assimilation.*

The striking investigations of Baly and his co-workers on the photocatalytic mechanism of the photosynthesis of carbohydrates<sup>1</sup> have now been extended to the production of nitrogen compounds;<sup>2</sup> this work is discussed later in this section. The photoelectric properties of chlorophyll, and their bearing on the electronic theory of sensitisation, have received further attention.<sup>3</sup> The energy changes accompanying carbon-dioxide assimilation (by the green alga, *Chlorella vulgaris*) in artificial light, and the percentage utilisation of energy in different parts of the spectrum have been studied.<sup>4</sup>

<sup>97</sup> D. W. Cutler, L. M. Crump, and H. Saudon, *Phil. Trans.*, 1922, [B], 211, 317.

<sup>98</sup> E. A. Mitscherlich, *Landw. Versuchs-Stat.*, 1922, 99, 133; A. Rippel, *J. Landw.*, 1922, 70, 9.

<sup>99</sup> E. J. Russell, *J. Min. Agric.*, 1922, 29, 752, 836.

<sup>1</sup> E. C. C. Baly, I. M. Heilbron, and W. F. Barker, *T.*, 1921, 119, 1025; see also E. C. C. Baly, *J. Soc. Dyers & Col.*, 1922, 38, 4; *A.*, i, 307.

<sup>2</sup> E. C. C. Baly, I. M. Heilbron, and D. P. Hudson, *T.*, 1922, 121, 1078.

<sup>3</sup> H. H. Dixon and N. G. Ball, *Sci. Proc. Roy. Dubl. Soc.*, 1922, 16, 435; *A.*, ii, 248.

<sup>4</sup> O. Warburg and E. Negelein, *Z. physikal. Chem.*, 1922, 102, 235; *A.*, i, 1097; C. Müller and O. Warburg, *Ber. Physikal.-Tech. Reichsanst.*, 1920, *A.*, i, 411.

Kostytshev has published a series of investigations<sup>5</sup> on photosynthesis. He finds that the ratio  $\text{CO}_2/\text{O}_2$  is disturbed in atmospheres containing abnormally large amounts of carbon dioxide, being first greater and then less than unity. In such atmospheres, leguminosæ assimilate markedly more carbon dioxide than other plants do. Assimilation is increased by the presence of nitrates in the soil. It has been shown that leaves of *Tropæolum majus* can assimilate formaldehyde vapour.<sup>6</sup> The supposed formation of hydrogen peroxide in the assimilation of carbon dioxide by plants<sup>7</sup> could not be confirmed,<sup>8</sup> neither could the statement<sup>9</sup> that leaves floating on sugar solution in sunlight are able to synthesise phloroglucinol be substantiated.<sup>10</sup> The possibility of obtaining substantial crop increases by artificial enrichment of the atmosphere by carbonic acid, which has aroused so much interest in Germany,<sup>11</sup> demands for its successful realisation that due regard be paid to the other controlling factors such as light, moisture, etc.<sup>12</sup>

#### *Carbohydrate Metabolism and Translocation.*

The disappearance of starch from leaves kept in the dark is favoured by dry conditions, and results in the production of non-reducing substances.<sup>13</sup> In the case of *Tropæolum majus*, sucrose seems to be the product formed.<sup>14</sup> The leaves of *Fagus sylvatica* and *Æsculus Hippocastanum*, however, when they turn yellow and die, suffer a diminution in their content of soluble carbohydrate, and an increase in their insoluble but readily hydrolysed carbohydrate.<sup>15</sup> From an investigation of the changes and movements of carbohydrates in *Mercurialis perennis* during its annual growth, it is concluded that there is another dextrorotatory substance present in addition to sucrose, though attempts to isolate it have so far failed.<sup>16</sup> The changes in the pectic constituents of apples during the ripening process have been investigated.<sup>17</sup> Soluble pectin is at a maximum when the fruit is ripe.

<sup>5</sup> G. Kostytshev, *Ber. Deut. bot. Gaz.*, 1921, **39**, 319, 328, 334; *A.*, i, 307, 308; *ibid.*, 1922, **40**, 112; *A.*, i, 613.

<sup>6</sup> M. Jacoby, *Biochem. Z.*, 1922, **128**, 119; *A.*, i, 502. <sup>7</sup> *A.*, 1918, ii, 107.

<sup>8</sup> H. Molisch, *ibid.*, 1921, **125**, 257; *A.*, i, 411.

<sup>9</sup> Waage, *Ber. Deut. bot. Ges.*, 1890, **8**, 250; *A.*, 1891, 605.

<sup>10</sup> M. Nierenstein, *Nature*, 1920, **105**, 391.

<sup>11</sup> *Ann. Reports*, 1921, **18**, 209.

<sup>12</sup> Densch, *Z. Pflanz. Düng.*, 1922, **1**, 32.

<sup>13</sup> H. Molisch, *Ber. Deut. bot. Ges.*, 1921, **39**, 339; *A.*, i, 309.

<sup>14</sup> H. Schroeder and T. Horn, *Biochem. Z.*, 1922, **130**, 165; *A.*, i, 906.

<sup>15</sup> R. Combes and D. Kohler, *Compt. rend.*, 1922, **175**, 590; *A.*, i, 1222.

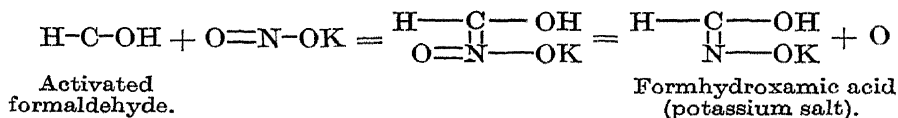
<sup>16</sup> P. Gillot, *J. Pharm. Chim.*, 1922, [vii], **26**, 250; *A.*, i, 1101.

<sup>17</sup> M. H. Carré, *Biochem. J.*, 1922, **16**, 704; *A.*, i, 1222; see also M. H. Carré and D. Haynes, *ibid.*, 60; *A.*, i, 401.

The quantitative investigation of the movements and changes of carbohydrates in plants would be much facilitated by the discovery of a quick and trustworthy method of starch estimation. A method which promises to satisfy these requirements has been described.<sup>18</sup>

### *Nitrogenous Assimilation and Metabolism.*

Very suggestive results have been obtained by Baly, Heilbron, and Hudson<sup>19</sup> in an extension of their work on photocatalysis to the formation of nitrogen compounds. Setting out from the observation of Schimper<sup>20</sup> that nitrites are always present in the living leaf in the dark, but that they disappear when the leaf is in the light, provided chlorophyll is present; and from the observation of Baudisch<sup>21</sup> that formhydroxamic acid is formed when an aqueous solution of potassium nitrite containing methyl alcohol is exposed to ultra-violet light, these investigators have shown that activated formaldehyde—such as is produced by the action of ultra-violet light of very short wave-length ( $\lambda = 200 \mu\mu$ ) on an aqueous solution of carbon dioxide, or of ordinary light on a similar solution containing a photocatalyst such as chlorophyll—readily combines with potassium nitrite to give formhydroxamic acid, which can at once react with more molecules of activated formaldehyde to produce a great variety of complex substances such as are found in the living plant. These reactions take precedence of the photocatalytic polymerisation of activated formaldehyde to form reducing sugars; the latter only occurs when the activated formaldehyde is produced at a rate greater than that at which it can react with potassium nitrite and with the formhydroxamic acid thus formed. These investigators have no doubt that formhydroxamic acid marks the first stage in the photosynthesis of the nitrogen compounds found in the plant. The reaction may be formulated thus :



They have obtained definite evidence of the formation of  $\alpha$ -amino-acids, of a crystalline alkaloidal base, of a crystalline base closely resembling and possibly identical with glyoxaline, and of a sub-

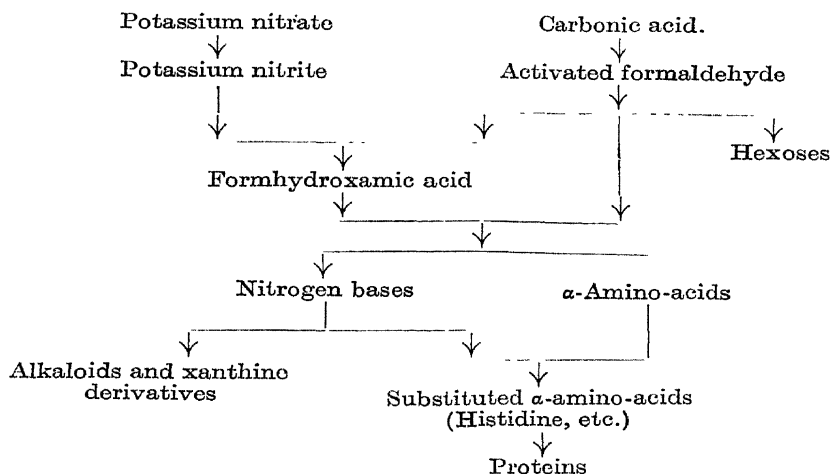
<sup>18</sup> A. R. Ling, *J. Inst. Brewing*, 1922, **28**, 838; *A.*, ii, 879.

<sup>19</sup> E. C. C. Baly, I. M. Heilbron, and D. P. Hudson, *loc. cit.*

<sup>20</sup> Schimper, *Bot. Z.*, 1888, **46**, 65.

<sup>21</sup> Baudisch, *Ber.*, 1911, **44**, 1009. For a recent summary of Baudisch's work, see *J. Biol. Chem.*, 1921, **48**, 489; *A.*, i, 194.

stituted  $\alpha$ -amino-acid which may be histidine. They show how the production of these, and of other nitrogenous plant products, by the interaction of activated formaldehyde and formhydroxamic acid, is readily explicable. The following scheme is put forward by them with some confidence as an indication of the main lines along which this photosynthesis takes place :



The far-reaching importance of this work can best be emphasised by the following quotation : <sup>22</sup>

“The activated formaldehyde produced by the photocatalytic action of chlorophyll on carbonic acid combines with the potassium nitrite known to be present in the leaves, this reaction taking precedence of all others. The formhydroxamic acid then condenses with more activated formaldehyde, this reaction taking second place in the order of precedence, whilst all excess of the activated formaldehyde polymerises to form hexoses.

“The interaction of the activated formaldehyde with formhydroxamic acid follows two main lines, the formation of amino-acids and of various nitrogen bases. These nitrogen bases consist of various types, namely, pyrrole, pyridine, and glyoxaline, which by further condensation with activated formaldehyde give indole, quinoline, isoquinoline, and xanthine derivatives. In cases where such is possible these bases condense with the amino-acids to give the substituted amino-acids such as histidine, tryptophan, etc. The excess of nitrogen bases undergoes further condensation to give alkaloids, whilst the substituted amino-acids interact to give proteins. The readiness with which all these reactions take place is due to the cardinal fact that the various compounds are produced

<sup>22</sup> E. C. C. Baly, I. M. Heilbron, and D. P. Hudson, *loc. cit.*, p. 1087.

in highly reactive phases, analogous to the highly reactive phase of formaldehyde when photosynthetically formed. This reactivity enables condensations to occur which are otherwise impossible to realise in the laboratory. It is a matter of common knowledge that these reactions must occur in the living plant, and our results show that the key to the problem is the enhanced reactivity of freshly synthesised molecules. . . . The synthesis of the nitrogen compounds found in the plant is not photosynthetic except in so far as the production of the activated formaldehyde by the chlorophyll is concerned. The various amino-acids, proteins, alkaloids, etc., are natural and indeed inevitable results of the photosynthesis of formaldehyde in the presence of potassium nitrite. . . .

" . . . . A further conclusion of importance is that the region where the synthesis occurs must necessarily be restricted to the leaves. Since it must not be forgotten that the synthesis of hexoses is taking place concurrently, the conditions are perfect for the formation of glucosides and we believe that the products of the nitrogen synthesis are translocated as soluble glucosides. The fact that nitrogen derivatives are found in other parts of the plant cannot be accepted as an argument that they must have been synthesised in those parts. There can be no doubt that the synthesis takes place in the leaves and that the compounds are subsequently distributed as soluble glucosides by the normal translocatory processes."

Ever since the classical experiments of Boussingault and of Lawes and Gilbert, it has been generally accepted that green plants are entirely dependent for nitrogen on the supplies they receive through their roots in the form of nitrates, ammonia, and possibly other forms, and that none can assimilate the elemental nitrogen of the air, although the leguminous plants are able to live in symbiosis with a nitrogen-fixing bacillus, and therefore are able to live without combined nitrogen from other sources. From time to time the claim has been advanced that green plants *are* able to fix nitrogen, but the evidence has never been free from suspicion. During the past year two further claims have been advanced, both from America. As already mentioned, one of these,<sup>23</sup> on behalf of the unicellular green algæ, is open to question. The other claim is on behalf of that possibly most investigated of all agricultural plants, the wheat plant. Only a preliminary note has so far appeared<sup>24</sup> and details will be awaited with great interest. Whilst no one would lightly deny the *possibility* of nitrogen fixation by green plants, the great bulk of agricultural experience is against

<sup>23</sup> F. B. Wann, *loc. cit.*

<sup>24</sup> C. B. Lipmann and J. K. Taylor, *Science*, 1922 56, 605.

the likelihood of its occurrence, and until conclusive and infallible evidence is advanced, the case remains as heretofore—"not proven."

Further work has been carried out on the nitrogenous metabolism of the runner bean;<sup>25</sup> one of the active enzymes appears to be asparaginase. In *Vicia sativa*, and also possibly in *Angelica silvestris* and *Trifolium pratense*, arginase is present.<sup>26</sup>

In general, the later nitrates are applied to cereals, the higher is the protein content, and the greater the hardness, of the grain.<sup>27</sup>

It is held that in the germinating seed of *Helianthus annuus* amino-acids and proteins are oxidised with formation of ammonia, which is used by the plant in the synthesis of asparagine and glutamine.<sup>28</sup>

For the formation of alkaloids by the blue and yellow lupines, nitrogenous fertilisers seem to be less suitable than the nitrogenous compounds produced by the nodule bacteria, judging by the alkaloid content of plants.<sup>29</sup> Ciamician and Ravenna have published a summary of their work since 1908 on the biological significance of alkaloids in plants.<sup>30</sup>

#### *Osmotic and Allied Phenomena.*

The permeability of plant cells, the imbibition of water by plant colloids, and similar osmotic processes undoubtedly have a fundamental bearing on the phenomena of root absorption, transpiration, translocation, etc. A considerable amount of work still appears on these topics,<sup>31</sup> but the subject is as yet in rather a confused state, and does not lend itself to brief discussion here. Mention may, however, be made of a suggestive article by Shull<sup>32</sup> on osmotic

<sup>25</sup> A. C. Chibnall, *Biochem. J.*, 1922, **16**, 344; *A.*, i, 908; *ibid.*, 599, 608; *A.*, i, 1225.

<sup>26</sup> A. Kiesel, *Z. physiol. Chem.*, 1922, **118**, 254, 267; *A.*, i, 412, 413.

<sup>27</sup> W. F. Gericke, *Soil Sci.*, 1922, **14**, 103; *A.*, i, 1226; see also *J. Amer. Soc. Agron.*, 1922, **14**, 311; also J. Davidson, *ibid.*, 118.

<sup>28</sup> A. Oparin, *Biochem. Z.*, 1921, **124**, 90; *A.*, i, 309.

<sup>29</sup> Vogel and E. Weber, *Z. Pflanz. Düng.*, 1922, [A], **1**, 85; *A.*, i, 798.

<sup>30</sup> C. Ciamician and C. Ravenna, *Biochem. therap. experim.*, 1922, **9**, 3; *A.*, i, 797.

<sup>31</sup> *Permeability*: W. J. V. Osterhout, *J. Gen. Physiol.*, 1921, **4**, 275; *A.*, i, 308; M. M. Brooks, *ibid.*, 347; *A.*, i, 308; H. Kahho, *Biochem. Z.*, 1921, **123**, 284; *A.*, i, 308; H. P. Möller, *Koll. Chem. Beihefte*, 1921, **14**, 97; *A.*, i, 95. *Imbibition*: D. T. MacDougall, *Proc. Amer. Phil. Soc.*, 1921, **60**, 15; *A.*, i, 204. *Root absorption*: G. M. Redfern, *Ann. Bot.*, 1922, **36**, 167; *A.*, i, 614; J. Stoklasa, *Biochem. Z.*, 1922, **128**, 35; *A.*, i, 502 (aluminium). *Effect of salts on plant protoplasm*: H. Kahho, *Biochem. Z.*, 1921, **117**, 87; *A.*, i, 94; *ibid.*, 1921, **120**, 125; *A.*, i, 205; *ibid.*, 1921, **122**, 39; *A.*, i, 311; W. Brenner, *Hyllningskrift tillägnad Ossian Aschan*, 1920, 36; *A.*, i, 907

<sup>32</sup> C. A. Shull, *Trans. Faraday Soc.*, 1922, **17**, 255.



phenomena in plants, and of a series of articles on permeability by Stiles.<sup>33</sup> The work of Priestley and his associates<sup>34</sup> is worthy of special mention.

### *Stimulant and Toxic Agents.*

The favourable action of calcium salts on germination appears to be concerned with the synthetic phase of this process.<sup>35</sup> Lead salts exert a toxic action on the plant. They accumulate in the roots, whose growth they especially hinder.<sup>36</sup> The oligodynamic effect of silver is due to the silver-ion; it can be neutralised by potassium cyanide, which converts the deleterious silver-ion into the  $\text{Ag}(\text{CN})_2$ -ion.<sup>37</sup>

It is stated that disodium arsenate has a stimulating action in low concentrations, although toxic if slightly higher concentrations are used.<sup>38</sup> This may, however, have been an indirect, soil effect.<sup>39</sup> Selenates, and particularly selenites, are markedly toxic to germination and growth of plants, as well as to *Azotobacter chroococcum*, but radium emanation is stimulating in its action on germination, and it inhibits the toxic action of selenates and selenites.<sup>40</sup> Sodium selenate at very low concentration is, however, stimulative to maize.<sup>41</sup>

Hippuric acid is toxic to plant cells at strengths above 0.09 per cent., but urea at 1 per cent. is harmless.<sup>42</sup> Cocaine and ecgonine are very much less toxic to *Lupinus albus* than they are to animals, but with sodium benzoate the reverse is the case.<sup>43</sup> From an investigation of the action of a large number of organic compounds it is concluded that, for compounds containing equal numbers of carbon atoms, the series: Amines, alcohols, aldehydes, acids, represents the order of diminishing toxicity towards plants.<sup>44</sup>

<sup>33</sup> W. Stiles, *New Phytologist*, 1922.

<sup>34</sup> J. H. Priestley, *ibid.*, 1922, 21, 41, 58, 62, 113, 210, 252.

<sup>35</sup> L. Maquenne and E. Demoussy, *Compt. rend.*, 1922, 175, 249; *A.*, i, 905.

<sup>36</sup> E. Bonnet, *ibid.*, 1922, 174, 488; *A.*, i, 412.

<sup>37</sup> R. Doerr and W. Berger, *Biochem. Z.*, 1922, 131, 151; *A.*, i, 1097; see also A. Luger, *ibid.*, 1921, 117, 153; *A.*, i, 65.

<sup>38</sup> J. Stewart and E. S. Smith, *Soil Sci.*, 1922, 14, 119; *A.*, i, 1222.

<sup>39</sup> See, for example, Rivière and Pichard, *loc. cit.*

<sup>40</sup> J. Stoklasa, *Compt. rend.*, 1922, 174, 1075; *A.*, i, 613; *Biochem. Z.*, 1922, 130, 604; *A.*, i, 974; B. Turina, *ibid.*, 1922, 129, 507; *A.*, i, 707 (also tellurium).

<sup>41</sup> J. Stoklasa, *Compt. rend.*, 1922, 174, 1256; *A.*, i, 614.

<sup>42</sup> T. Bokorny, *Biochem. Z.*, 1922, 132, 197; *A.*, i, 1222.

<sup>43</sup> D. I. Macht and M. B. Livingston, *J. Gen. Physiol.*, 1922, 4, 573; *A.*, i, 798.

<sup>44</sup> G. Ciamician and A. Galizzi, *Gazzetta*, 1922, 52, i, 3; *A.*, i, 503.

The toxic action of traces of coal gas on plants is due to unsaturated hydrocarbons (ethylene), which appear to act specially in preventing normal root development.<sup>45</sup>

The stimulating effect of the electric discharge appears to be definitely established by field experiments on spring-sown oats and barley, but this problem is still under investigation.<sup>46</sup>

### *Plant Constituents and Products.*

#### *Inorganic Constituents.*

Manganese, which appears to be an invariable constituent of plants,<sup>47</sup> is found in the greatest quantities in those parts of the plant such as the seeds, and young leaves where the chemical changes are most intense.<sup>48</sup> It has been found,<sup>49</sup> using many different species of plants, that in a medium entirely free from manganese growth ceases, and the plants become chlorotic, after six or eight weeks, by which time the manganese originally contained in the seed is presumably no longer sufficient. It is suggested that manganese is necessary for chlorophyll formation, and that it is concerned in nitrogen assimilation and protein synthesis, since leguminous plants are more sensitive to its absence.

Minute traces of nickel, and, with two exceptions, of cobalt, have been found in sixteen different species of common plants.<sup>50</sup> These two elements have also been found in minute amounts in two arable soils.<sup>51</sup> From the fact that the amount of nickel is much greater than that of cobalt both in the soils and in the plants examined it seems that the occurrence of these elements in the plant may be merely adventitious.

Chlorine occurs in most plants, always as chloride; it is most abundant in succulent parenchymatous tissues. Conifers, mosses, ferns, epiphytes, parasites, and saprophites contain little or no chlorine.<sup>52</sup> Fluorine is a normal constituent of Spanish grapes.<sup>53</sup>

<sup>45</sup> J. H. Priestley, *Ann. Appl. Biol.*, 1922, **9**, 146; see also C. Wehmer, *Bied. Zentr.*, 1921, **50**, 425; *A.*, i, 211.

<sup>46</sup> *J. Min. Agric.*, 1922, **29**, 792.

<sup>47</sup> D. H. Wester, *Biochem. Z.*, 1921, **118**, 158; *A.*, i, 94; *Pharm. Weekblad.*, 1922, **59**, 51; *A.*, i, 309; G. Bode and K. Hembd, *Biochem. Z.*, 1921, **124**, 84; *A.*, i, 415.

<sup>48</sup> G. Bertrand and M. Rosenblatt, *Compt. rend.*, 1921, **173**, 1118; *A.*, i, 95; *ibid.*, 1922, **174**, 491; *A.*, i, 411; F. Jadin and A. Astruc, *Bull. Soc. chim.*, 1922, **31**, 917; *A.*, i, 1098.

<sup>49</sup> J. S. McHargue, *J. Amer. Chem. Soc.*, 1922, **44**, 1592; *A.*, i, 906.

<sup>50</sup> G. Bertrand and M. Mokragatz, *Compt. rend.*, 1922, **175**, 458; *A.*, i, 1099.

<sup>51</sup> *Idem, ibid.*, 112; *A.*, i, 975.

<sup>52</sup> J. Jung, *Sitzungsber. Akad. Wiss.*, 1920, **129**, 297; *A.*, i, 1098.

<sup>53</sup> M. L. Pondal, *Anal. Asoc. Quím. Argentina*, 1922, **10**, 57; *A.*, i, 1100.

The amount and distribution of inorganic and organic phosphates in various seeds have been studied.<sup>54</sup> Marine algæ generally appear to contain a small amount of arsenic.<sup>55</sup>

### *Organic Plant Products.*

Chemical work on the constitution of plant products comes within the scope of the Reports on organic chemistry, and is not considered in this Report; in this section, attention is confined to the occurrence of the different classes of organic substances in plants, and to work throwing light on the mode of formation of special classes of plant products.

*Carbohydrates and Glucosides.*—The sugars of wheat straw,<sup>56</sup> and the hemicelluloses of the seed of *Asparagus officinalis*<sup>57</sup> have been examined. Cytopenantans is the name proposed for the "hemicellulose"-like constituents of the cell-walls of plants.<sup>58</sup> An improved method for the preparation of raffinose from cotton-seed meal has been described.<sup>59</sup> Papers have appeared on the occurrence and nature of the sugars and glucosides in *Sedum Telephium* (glucoside of an essential oil),<sup>60</sup> *Melampyrum arvense* (aucubin),<sup>61</sup> *Rhinanthus Crista-Galli* (aucubin),<sup>62</sup> several species of *Orchis*,<sup>63</sup> in the *Schrophulariaceæ*,<sup>64</sup> the *Caryophyllaceæ* and *Papilionaceæ*,<sup>65</sup> and in *Viburnum opulus*, extracts of red *Cinchona*, and the Cola nut.<sup>66</sup> Chinese tannin,<sup>67</sup> oak tannin,<sup>68</sup> and a crystalline tannin from *Acer ginnala*<sup>69</sup> have been studied. Saponins have been isolated from

<sup>54</sup> F. Rogozinski, *Bull. Acad. Sci. Cracovie*, 1915, [B], No. 5, 87; A., i, 1226.

<sup>55</sup> A. J. Jones, *Pharm. J.*, 1922, 109, 86; A., i, 905.

<sup>56</sup> S. H. Collins and B. Thomas, *J. Agric. Sci.*, 1922, 12, 280; S. H. Collins, *J. Soc. Chem. Ind.*, 1922, 41, 56r; A., ii, 323.

<sup>57</sup> W. E. Cake and H. H. Bartlett, *J. Biol. Chem.*, 1922, 51, 93; A., i, 504.

<sup>58</sup> D. H. F. Clayson, F. W. Norris, and S. B. Schryver, *Biochem. J.*, 1921, 15, 643; A., i, 206.

<sup>59</sup> E. P. Clark, *J. Amer. Chem. Soc.*, 1922, 44, 210; A., i, 323.

<sup>60</sup> M. Bridel, *Bull. Soc. Chim. biol.*, 1922, 4, 242; A., i, 799; *J. Pharm. chim.*, 1922, [vii], 26, 289; A., i, 1225.

<sup>61</sup> M. Bridel and M. Braecke, *ibid.*, 1922, 25, 449; A., i, 799; *Compt. rend.*, 1921, 173, 1403; A., i, 209.

<sup>62</sup> *Idem*, *ibid.*, 1922, 175, 532; A., i, 1225; see also *ibid.*, 640; A., i, 1168.

<sup>63</sup> H. Hérissé and P. Delauney, *Bull. Soc. Chim. biol.*, 1921, 3, 573; A., i, 210.

<sup>64</sup> M. Braecke, *ibid.*, 1922, 4, 407; A., i, 1225.

<sup>65</sup> C. Vergelot, *ibid.*, 1921, 3, 513; A., i, 207.

<sup>66</sup> R. Arnold, *ibid.*, 547; A., i, 311.

<sup>67</sup> K. Freudenberg, *Ber.*, 1922, 55, [B], 2813; A., i, 1169.

<sup>68</sup> K. Freudenberg and E. Vollbrecht, *ibid.*, 2420; A., i, 1046.

<sup>69</sup> A. G. Perkin and Y. Uyeda, *T.*, 1922, 121, 66.

*Agave lechuguilla* <sup>70</sup> and *Aralia Montana*, <sup>71</sup> and the effect of daylight on the content of active material in *Digitalis* has been examined. <sup>72</sup>

*Acids and Esters.*—The occurrence is recorded of citric and malic acids in *Ribes rubrum*; <sup>73</sup> of methyl anthranilate in grape juice; <sup>74</sup> of lactic acid in *Rubus idæus* (with succinic acid), <sup>75</sup> *R. fruticosus*, <sup>76</sup> *Papaver somniferum*, *Ricinus communis*, and *Agave Sisalana*; <sup>77</sup> of oxalic acid in *Acacia cambagei* (as calcium salt), <sup>78</sup> and in the leaves of elder, hawthorn, horse-chestnut, and barley; <sup>79</sup> and of malic acid in *Pyrus coronaria*, *Rhus glabra* (with gallic acid), *Acer saccharum*, <sup>80</sup> *Prunus avium*, <sup>81</sup> and *Pyrus aucuparia*. <sup>82</sup> The third optically active form of malic acid said to be present in certain plants does not exist. <sup>83</sup> Various esters have been identified in peaches. <sup>84</sup>

*Triglycerides; Essential Oils.*—A large number of plants and vegetable products have been examined as to their content of substances of these classes; it would, however, be neither useful nor practicable in the space available to give details here. The index of the *Journal* for 1922 should be referred to.

*Pigments.*—Despite the definite evidence produced by Willstätter and others, that anthocyanins are reduction products of flavones, <sup>85</sup> the known correlation of distribution of oxydases and of anthocyanins continues to be used as an argument for the older oxidation hypothesis. <sup>86</sup> It seems difficult to avoid the impression that oxidation is indeed a factor in anthocyanin formation, but it is quite

<sup>70</sup> C. O. Johns, L. H. Chernoff, and A. Viehoveer, *J. Biol. Chem.*, 1922, 52, 335; *A.*, i, 797.

<sup>71</sup> A. W. van der Haar, *Ber.*, 1922, 55, [B], 3041; *A.*, i, 1168.

<sup>72</sup> O. von Dafert, *Bied. Zentr.*, 1921, 50, 422; *A.*, i, 97.

<sup>73</sup> H. Franzen and E. Schumacher, *Z. physiol. Chem.*, 1921, 115, 9; *A.*, i, 310.

<sup>74</sup> F. B. Power and V. K. Chesnut, *J. Amer. Chem. Soc.*, 1921, 43, 1741; *A.*, i, 97.

<sup>75</sup> H. Franzen and E. Stern, *Z. physiol. Chem.*, 1922, 121, 195; *A.*, i, 975.

<sup>76</sup> H. Franzen and E. Keyssner, *ibid.*, 1921, 116, 166; *A.*, i, 310.

<sup>77</sup> H. Franzen and E. Stern, *ibid.*, 1921, 115, 270; *A.*, i, 311.

<sup>78</sup> T. Steel, *Chem. News*, 1921, 123, 315; *A.*, i, 310.

<sup>79</sup> A. Bau, *Z. tech. Biol.*, 1921, 8, 151; *A.*, i, 309.

<sup>80</sup> C. E. Sando and H. H. Bartlett, *J. Agric. Res.*, 1921, 22, 221; *A.*, i, 100.

<sup>81</sup> H. Franzen and F. Helwert, *Z. physiol. Chem.*, 1922, 122, 46; *A.*, i, 1102.

<sup>82</sup> H. Franzen and R. Ostertag, *ibid.*, 1922, 119, 150; *A.*, i, 116.

<sup>83</sup> *Idem*, *ibid.*, 1922, 122, 263; *A.*, i, 1223.

<sup>84</sup> F. B. Power and V. K. Chesnut, *J. Amer. Chem. Soc.*, 1921, 43, 1725; *A.*, i, 99.

<sup>85</sup> See, for example, J. Costantin, *Ann. Sci. Nat. Bot.*, 1919, [x], 1, 38; *A.*, i, 162.

<sup>86</sup> M. Mirande, *Compt. rend.*, 1922, 175, 595, 711; *A.*, i, 1224.

possible that the two views may be reconciled on the assumption that oxidation is needed in the earlier stages of the synthesis, and that only the final stage is one of reduction of flavone derivative to anthocyanin. The work of St. Jonesco<sup>87</sup> on anthocyanins, a feature of which is his support of the oxidation hypothesis, is held by Combes<sup>88</sup> to be invalidated by the fact that his (St. Jonesco's) materials are not  $\gamma$ -pyrone pigments but only tannins. The sap pigment of the beet root is stated to be produced by oxidation of a colourless chromogen.<sup>89</sup>

The presence of cyanin in the rose<sup>90</sup> and of pelargonin in the scarlet pelargonium<sup>91</sup> has been confirmed by their isolation from varieties not hitherto examined.

The colouring matters of *Lithospermum erythrorhizon*,<sup>92</sup> and of several species of the *Schizophyceæ*<sup>93</sup> have been examined. It is stated that a new class of glucosidal yellow pigments—"anthochlor"—is represented in many plants.<sup>94</sup>

*Plant Proteins.*—The chemical interpretation of differences in the quality of agricultural products is a comparatively untouched field, of great importance. A suggestive investigation<sup>95</sup> on the difference between the "strong" Canadian wheats and the "weak" English wheats has brought out the interesting fact that there is a difference between the glutenins of these two wheats, which is manifested by an examination of their racemisation curves. The proteins of the Adzuki bean (*Phaseolus angularis*),<sup>96</sup> the Lima bean (*P. lunatus*),<sup>97</sup> of the seed of the tomato,<sup>98</sup> of buckwheat,<sup>99</sup> lucerne,<sup>1</sup> *Sorghum vulgare*,<sup>2</sup> and of cotton seed meal, the soja bean, and the cocoa-nut<sup>3</sup> have been examined.

<sup>87</sup> St. Jonesco, *Compt. rend.*, 1921, **173**, 850, 1006; *A.*, i, 97; *ibid.*, 1922, **174**, 1635; *A.*, i, 797; *ibid.*, 1922, **175**, 592; *A.*, i, 1224.

<sup>88</sup> R. Combes, *ibid.*, 1921, **174**, 58; *A.*, i, 206; *ibid.*, 1922, **174**, 240; *A.*, i, 412.

<sup>89</sup> A. Kozłowski, *ibid.*, 1921, **173**, 855; *A.*, i, 97.

<sup>90</sup> G. Currey, *Proc. Roy. Soc.*, 1922, [B], **93**, 194; *A.*, i, 413.

<sup>91</sup> G. Currey, *T.*, 1922, **121**, 319.

<sup>92</sup> R. Majima and C. Kuroda, *Acta Phytochim.*, 1922, **1**, 43; *A.*, i, 946.

<sup>93</sup> K. Boresch, *Biochem. Z.*, 1921, **119**, 166; *A.*, i, 210.

<sup>94</sup> G. Klein, *Sitzungsber. Akad. Wiss. Wien*, 1920, **129**, 341; *A.*, i, 1099.

<sup>95</sup> H. E. Woodman, *J. Agric. Sci.*, 1922, **12**, 231.

<sup>96</sup> D. B. Jones, A. J. Finks, and C. E. F. Gersdorff, *J. Biol. Chem.*, 1922, **51**, 103; *A.*, i, 504.

<sup>97</sup> D. B. Jones, C. E. F. Gersdorff, C. O. Johns, and A. J. Finks, *ibid.*, 1922, **53**, 231; *A.*, i, 1101.

<sup>98</sup> C. O. Johns and C. E. F. Gersdorff, *ibid.*, 1922, **51**, 439; *A.*, i, 800.

<sup>99</sup> A. Kiesel, *Z. physiol. Chem.*, 1922, **118**, 301; *A.*, i, 412.

<sup>1</sup> T. B. Osborne, J. Wakeman, and C. S. Leavenworth, *J. Biol. Chem.*, 1921, **49**, 63; *A.*, i, 99; *ibid.*, 1922, **53**, 411; *A.*, i, 1104; H. G. Miller, *J. Amer. Chem. Soc.*, 1921, **43**, 2656; *A.*, i, 414.

<sup>2</sup> S. Visco, *Arch. Farm. sperim. Sci. aff.*, 1921, **31**, 173; *A.*, i, 211.

<sup>3</sup> W. G. Friedemann, *J. Biol. Chem.*, 1922, **51**, 17; *A.*, i, 505.

*Plant Bases.*—The alkaloid of the yew (*Taxus baccata*) has been isolated<sup>4</sup> and the relations between the alkaloids of the calumba root have been elucidated.<sup>5</sup> The alkaloid content of belladonna plants is increased by keeping them in the dark.<sup>6</sup> Natural muscarine has now been isolated in the pure state from *Amanita muscaria*, and it has been shown to be a base of greater complexity than choline or betainealdehyde.<sup>7</sup>

*General.*—The composition of a large number of other plants has been studied, but it is not possible to give details here. The index of the *Journal* for 1922 should be consulted.

### *The Chemistry of Fermentation and Enzyme Action.*

It is not possible in the remaining space to deal with this subject fully. A brief survey of last year's work in this field, which makes no pretence to be exhaustive, will be given; a full discussion of the subject is reserved for a later occasion. Useful reviews of recent German work were given at the recent meeting of the Naturforscherversammlung at Leipzig.<sup>7a</sup>

*Fermentation of Carbohydrates and Allied Substances.*—Neuberg's view as to the importance of pyruvic acid in fermentation, although challenged,<sup>8</sup> has received further confirmation.<sup>9</sup> Fernbach has published a useful review of present views on the rôle of acetaldehyde.<sup>10</sup> Neuberg's second mode of fermentation has now been realised with various fungi<sup>11</sup> and with carbohydrates other than glucose.<sup>12</sup> Patents for the industrial preparation of glycerol by fermentation have now been published.<sup>13</sup> The third and fourth forms of fermentation, by which acetic and butyric acids are produced, as well as various other types of acid fermentation, have

<sup>4</sup> E. Winterstein and D. Iatrides, *Z. physiol. Chem.*, 1921, **117**, 240; *A.*, i, 572.

<sup>5</sup> E. Späth and K. Böhm, *Ber.*, 1922, **55**, [B], 2985; *A.*, i, 1174.

<sup>6</sup> J. Ripert, *Compt. rend.*, 1921, **173**, 928; *A.*, i, 96.

<sup>7</sup> H. King, *T.*, 1922, **121**, 1743.

<sup>7a</sup> H. von Euler, *Ber.*, 1922, **55**, [B], 3583; R. Willstätter, *ibid.*, 3601; C. Neuberg, *ibid.*, 3624.

<sup>8</sup> J. Kerb and K. Zeckendorf, *Biochem. Z.*, 1921, **122**, 307; *A.*, i, 305.

<sup>9</sup> M. von Grab, *ibid.*, 1921, **123**, 69; *A.*, i, 306.

<sup>10</sup> A. Fernbach and M. Schoen, *Bull. Inst. Pasteur*, 1920, **18**, 385; *A.*, i, 203.

<sup>11</sup> C. Neuberg and C. Cohen, *Biochem. Z.*, 1921, **122**, 204; *A.*, i, 304.

<sup>12</sup> M. Tomita, *ibid.*, 1921, **121**, 164; *A.*, i, 307; see also H. Kumagawa, *ibid.*, 1922, **131**, 148; *A.*, i, 972; E. Abderhalden, *Fermentforsch.*, 1921, **5**, 89, 110; *A.*, i, 92; O. Fernández and T. Garmendia, *Anal. Fís. Quím.*, 1921, **19**, 313; *A.*, i, 405.

<sup>13</sup> Vereinigte Chemische Werke Akt.-Ges., D.R.-P. 343321 and 347604; *A.*, i, 980.

evoked considerable research.<sup>14</sup> The curious action of carboligase has been further studied,<sup>15</sup> also the fermentation of lactic acid by yeast.<sup>16</sup> The stimulating<sup>17</sup> and toxic<sup>18</sup> effects of various agents on yeast fermentation and on various bacteria,<sup>19</sup> and moulds<sup>20</sup> have been studied. The claim that fermentation can be effected by mixtures containing peptone,<sup>21</sup> although contested,<sup>22</sup> appears to be justified, it being stated that dextrose is converted quantitatively by peptone at 37° into inactive lactic acid, using sodium bicarbonate as a buffer.<sup>23</sup>

The fermentation of inulin by *Monilia macedoniensis* may be used in a scheme for the identification of that carbohydrate by a mycological method.<sup>24</sup> In the attack of pentoses by moulds,

<sup>14</sup> *Acetic acid*: H. Kumagawa, *Biochem. Z.*, 1921, **123**, 225; *A.*, i, 305; E. Aubel, *Compt. rend.*, 1921, **173**, 1493; *A.*, i, 201. *Butyric acid*: C. Neuberg and B. Arinstein, *Biochem. Z.*, 1921, **117**, 269; *A.*, i, 91; M. M. Brooks, *J. Gen. Physiol.*, 1921, **4**, 177; *A.*, i, 201. *Lactic acid*: W. H. Peterson, E. B. Fred, and J. H. Anderson, *J. Biol. Chem.*, 1922, **53**, 111; *A.*, i, 971; O. R. Brunkow, W. H. Peterson, and E. B. Fred, *J. Amer. Chem. Soc.*, 1921, **43**, 2244; *A.*, i, 312 (Sauerkraut). *Silage*: A. Amos and H. E. Woodman, *J. Agric. Sci.*, 1922, **12**, 337. *Inositol fermentation*: J. A. Hewitt and D. B. Steabben, *Biochem. J.*, 1921, **15**, 665; *A.*, i, 406; H. Kumagawa, *Biochem. Z.*, 1922, **131**, 157; *A.*, i, 972. *Citromyces*: W. Butkewitsch, *ibid.* 1922, **129**, 455, 464; *A.*, i, 707; *ibid.*, 1922, **131**, 327, 338; *A.*, i, 973. *Other acids*: T. Yabuta, *J. Chem. Soc. Tokyo*, 1916, **37**, 1185, 1234; *A.*, i, 939 (*Aspergillus oryzae*); M. Molliard, *Compt. rend.*, 1922, **174**, 881; *A.*, i, 611 (*Aspergillus niger*). *Acetone and butyl alcohol*: G. C. Robinson, *J. Biol. Chem.*, 1922, **53**, 125; *A.*, i, 971.

<sup>15</sup> C. Neuberg and L. Liebermann, *Biochem. Z.*, 1921, **121**, 311; *A.*, i, 305; J. Hirsch, *ibid.*, 1922, **131**, 178; *A.*, i, 973.

<sup>16</sup> O. Fürth and F. Lieben, *ibid.*, 1922, **128**, 144; *A.*, i, 502; *ibid.*, 1922, **132**, 165; *A.*, i, 1219; F. Lieben, *Oesterr. Chem. Ztg.*, 1922, **25**, 87; *A.*, i, 796.

<sup>17</sup> C. Neuberg, E. Reinfurth, and M. Sandberg, *Biochem. Z.*, 1921, **121**, 215; *A.*, i, 306; *ibid.*, 1921, **125**, 202; *A.*, i, 408; *ibid.*, 1921, **126**, 153; *A.*, i, 408; H. von Euler and S. Karlsson, *ibid.*, 1922, **130**, 550; *A.*, i, 972; P. Mayer, *ibid.*, 1922, **131**, 1; *A.*, i, 972; E. Lindberg, *ibid.*, 1922, **132**, 110; *A.*, i, 1219; T. Tholin, *Z. physiol. Chem.*, 1921, **115**, 235; *A.*, i, 305.

<sup>18</sup> H. Plagge, *Biochem. Z.*, 1921, **118**, 129; *A.*, i, 93; F. Boas, *ibid.*, 1921, **117**, 166; *A.*, i, 94; *ibid.*, 1922, **129**, 144; *A.*, i, 613; R. Somogyi, *ibid.*, 1921, **120**, 100; *A.*, i, 201.

<sup>19</sup> R. Cobet and V. van der Reis, *ibid.*, 1922, **129**, 73; *A.*, i, 611 (arsenic); L. E. Walbum, *Compt. rend. Soc. Biol.*, 1921, **85**, 619; *A.*, i, 795 (manganese); T. Duboc, *Compt. rend.*, 1922, **175**, 326; *A.*, i, 972; G. Joachimoglu, *Z. Urol.*, 1922, **16**, 97; *A.*, i, 1095; Laborde, Jaloustre, and M. Leulier, *Bull. Soc. Chim. biol.*, 1922, **4**, 415; *A.*, i, 1219.

<sup>20</sup> L. Plantefol, *Compt. rend.*, 1922, **174**, 123; *A.*, i, 204.

<sup>21</sup> E. Baur and E. Herzfeld, *Biochem. Z.*, 1921, **117**, 96; *A.*, i, 93; *ibid.*, 1922, **131**, 382; *A.*, i, 1097.

<sup>22</sup> A. Bau, *ibid.*, 1921, **122**, 306; *A.*, i, 307.

<sup>23</sup> G. Schlatter, *ibid.*, 1922, **131**, 362; *A.*, i, 1096.

<sup>24</sup> A. Castellani and F. E. Taylor, *Biochem. J.*, 1922, **16**, 655; *A.*, ii, 879.

practically the whole of the carbon consumed can be accounted for as carbon dioxide and mycelium.<sup>25</sup> *Aspergillus glaucus* converts glycerol into the methyl ether of a substance,  $C_6H_6O_4$ , which is probably a  $\gamma$ -pyrone derivative similar to maltol.<sup>26</sup> The ability of *Fusarium lini* to utilise various carbohydrates and acids has been studied,<sup>27</sup> also the energy yield of the growth of *Aspergillus niger* on dextrose,<sup>28</sup> which works out at 66—70 per cent. of that of the dextrose consumed after allowing for the maintenance requirements.

### *Carbohydrate-splitting Enzymes.*

Willstätter is making a mass attack on the chemistry of enzymes and of enzyme action, and has published several lengthy papers on invertase,<sup>29</sup> raffinase,<sup>30</sup> maltase,<sup>31</sup> lactase,<sup>32</sup> and emulsin.<sup>33</sup> Although Willstätter's masterly successes in other fields of plant chemistry justify one in anticipating important results from this work, it is still in its infancy, and has not yet reached the stage when any broad generalisations emerge.

The influence of conditions on the activity of the amylases present in malt, pancreatic extract, and saliva,<sup>34</sup> and in *Aspergillus niger*<sup>35</sup> has been investigated. Euler has published several further papers on saccharase,<sup>36</sup> and this enzyme has also been studied by several

<sup>25</sup> W. H. Peterson, E. B. Fred, and E. G. Schmidt, *J. Biol. Chem.*, 1922, 54, 19; *A.*, i, 1220.

<sup>26</sup> F. Traetta-Mosca and M. Preti, *Gazzetta*, 1921, 51, ii, 269; *A.*, i, 91.

<sup>27</sup> Y. Tochinal, *Ann. Phytopath. Soc. Japan*, 1920, 1, 22; *A.*, i, 207.

<sup>28</sup> E. E. Terroine and R. Wurmser, *Compt. rend.*, 1922, 174, 1435; *A.*, i, 706.

<sup>29</sup> R. Willstätter and F. Racke, *Annalen*, 1922, 427, 111; *A.*, i, 598; R. Willstätter, J. Graser, and R. Kuhn, *Z. physiol. Chem.*, 1922, 123, 1; *A.*, i, 1200.

<sup>30</sup> R. Willstätter and R. Kuhn, *ibid.*, 1922, 115, 180; *A.*, i, 284.

<sup>31</sup> R. Willstätter and W. Steibelt, *ibid.*, 1921, 115, 199; *A.*, i, 282; *ibid.*, 211; *A.*, i, 306; R. Willstätter and R. Kuhn, *ibid.*, 1921, 116, 53; *A.*, i, 283.

<sup>32</sup> R. Willstätter and G. Oppenheimer, *ibid.*, 1922, 118, 168; *A.*, i, 203.

<sup>33</sup> R. Willstätter and W. Csányi, *ibid.*, 1921, 117, 172; *A.*, i, 390; R. Willstätter and G. Oppenheimer, *ibid.*, 1922, 121, 183; *A.*, i, 959.

<sup>34</sup> D. Maestrini, *Arch. Farm. sperim. Sci. aff.*, 1921, 32, 40, 49, 99, 126; *A.*, i, 507, 508; R. Lecoq, *J. Pharm. Chim.*, 1922, 25, 18; *A.*, i, 312; F. Ducháček, *Chem. Listy*, 1922, 16, 202; *A.*, i, 974; H. C. Sherman, *Carnegie Inst. Washington Yearbook*, 1919, 18, 328; *A.*, i, 66; H. C. Sherman and M. Wayman, *J. Amer. Chem. Soc.*, 1921, 43, 2454; *A.*, i, 282; H. C. Sherman and F. Walker, *ibid.*, 2461; *A.*, i, 283; U. Olsson, *Z. physiol. Chem.*, 1921, 117, 91; *A.*, i, 390; E. Ernström, *ibid.*, 1922, 119, 190; *A.*, i, 599.

<sup>35</sup> G. L. Funke, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, 25, 6; *A.*, 796.

<sup>36</sup> H. v. Euler and Svanberg, *Z. physiol. Chem.*, 1921, 114, 137; *A.*, i, 284; H. v. Euler and K. Myrbäck, *ibid.*, 1922, 120, 61; *A.*, i, 693; H. v. Euler and D. Svanberg, *Arkiv Kem. min. Geol.*, 1922, 8, No. 12, 1; *A.*, i, 1200; H. v. Euler and K. Myrbäck, *ibid.*, No. 17, 1; *A.*, i, 1201.



other investigators.<sup>37</sup> The hydrolytic<sup>38</sup> and synthetic<sup>39</sup> actions of emulsin have been investigated, and the isolation of active preparations of this enzyme has been described.<sup>40</sup> Emulsin is present in a new species of yeast, *Willia javanica*.<sup>41</sup> Various species of *Rhizopus* contain a pectinase.<sup>42</sup> The preparation of tannase from a mould has been described.<sup>43</sup>

Saccharophosphatase has been found in the seeds of the higher cultivated plants and in the leaves of the potato.<sup>44</sup> The "insoluble" amylase of barley has been shown by an ingenious method<sup>45</sup> to be associated with the alcohol-soluble group of proteins (hordein).

### *Degradation of Proteins and Amino-acids.*

Papers have appeared on the degradation of proteins by yeast,<sup>46</sup> on the proteolytic enzymes of malt,<sup>47</sup> and on the bacterial degradation of leucine,<sup>48</sup> tyrosine,<sup>49</sup> tryptophan,<sup>50</sup> and  $\alpha$ -naphthylalanine.<sup>51</sup>

### *Other Enzymes.*

A method for the preparation of castor bean lipase has been described and its action studied.<sup>52</sup> Lipase was also found in a

<sup>37</sup> W. C. Vosburgh, *J. Amer. Chem. Soc.*, 1921, **43**, 1693; *A.*, i, 64; E. W. Miller, *J. Biol. Chem.*, 1921, **43**, 329; *A.*, i, 203; J. M. Nelson and D. I. Hitchcock, *J. Amer. Chem. Soc.*, 1921, **43**, 1956; *A.*, i, 184; *ibid.*, 2632; *A.*, i, 388; H. Colin and A. Chaudun, *Compt. rend.*, 1922, **174**, 218; *A.*, i, 389; A. Chaudun, *J. Fabr. Sucre*, 1921, **62**, No. 39; *A.*, i, 389; S. Kostyshev and P. Eliasberg, *Z. physiol. Chem.*, 1922, **118**, 233; *A.*, i, 410; E. Canals, *Bull. Soc. chim.*, 1922, [iv], **31**, 921; *A.*, i, 1075.

<sup>38</sup> J. Giaja, *J. Chim. Physique*, 1921, **19**, 77; *A.*, i, 185.

<sup>39</sup> L. Rosenthaler, *Fermentforsch.*, 1922, **5**, 334; *A.*, i, 480; E. Nordefeldt, *Biochem. Z.*, 1921, **118**, 15; *A.*, i, 66.

<sup>40</sup> B. Helferich, *Z. physiol. Chem.*, 1921, **117**, 159; *A.*, i, 390.

<sup>41</sup> J. Groenewege, *Mededeel. Algemeen Proefsta. voor den Landbouw*, 1921, No. 9, 1; *A.*, i, 903.

<sup>42</sup> L. L. Harter and J. H. Weimer, *J. Agric. Research*, 1921, **21**, 609; *A.*, i, 507.

<sup>43</sup> K. Freudenberg and E. Vollbrecht, *Z. physiol. Chem.*, 1921, **116**, 277, *A.*, i, 285.

<sup>44</sup> A. Némec and F. Duchoň, *Biochem. Z.*, 1921, **119**, 73; *A.*, i, 206.

<sup>45</sup> J. L. Baker and H. F. E. Hulton, *T.*, 1922, **121**, 1929.

<sup>46</sup> N. N. Ivanov, *Biochem. Z.*, 1921, **120**, 1, 25, 62; *A.*, i, 202, 206; W. Dieter, *Z. physiol. Chem.*, 1922, **120**, 281; *A.*, i, 795; E. Abderhalden and E. Wertheimer, *Fermentforsch.*, 1922, **6**, 1; *A.*, i, 796.

<sup>47</sup> H. Lundin, *Biochem. Z.*, 1922, **131**, 193; *A.*, i, 959.

<sup>48</sup> M. Arai, *ibid.*, 1921, **122**, 251; *A.*, i, 303.

<sup>49</sup> F. Sieke, *Z. Hyg.*, 1921, **94**, 214; *A.*, i, 902.

<sup>50</sup> T. Sasaki and I. Otsuka, *Biochem. Z.*, 1921, **121**, 167; *A.*, i, 302.

<sup>51</sup> T. Sasaki and J. Kinose, *ibid.*, 171; *A.*, i, 303.

<sup>52</sup> D. E. Haley and J. F. Lyman, *J. Amer. Chem. Soc.*, 1921, **43**, 2664; *A.*, i, 390.

strain of *Aspergillus niger*.<sup>53</sup> The production of fat from carbohydrate by the enzymes of oil seeds,<sup>54</sup> by yeast,<sup>55</sup> and by the timothy grass bacillus<sup>56</sup> has been investigated.

Other papers deal with the properties<sup>57</sup> and occurrence<sup>58</sup> of urease.

It is suggested that the catalase activity of seeds may be used as an indication of their germinative capacity.<sup>59</sup>

H. J. PAGE.

<sup>53</sup> R. Schenker, *Biochem. Z.*, 1921, **120**, 164; *A.*, i, 203.

<sup>54</sup> L. Spiegel, *Z. physiol. Chem.*, 1922, **120**, 103; *A.*, i, 694.

<sup>55</sup> I. S. Maclean, *Biochem. J.*, 1922, **16**, 370; *A.*, i, 795.

<sup>56</sup> M. Stephenson and M. D. Whetham, *Proc. Roy. Soc.*, 1922, [B], **93**, 262; *A.*, i, 500.

<sup>57</sup> S. Lövgren, *Biochem. Z.*, 1921, **119**, 215; *A.*, i, 185; D. H. Wester, *Pharm. Weekblad*, 1922, **59**, 173; *A.*, i, 391.

<sup>58</sup> A. Goris and P. Costy, *Compt. rend.*, 1922, **175**, 539; *A.*, i, 1220.

<sup>59</sup> A. Němec and F. Duchoň, *ibid.*, 1921, **173**, 933; *A.*, i, 94; *ibid.*, 1922, **174**, 632; *A.*, i, 411. But see J. de Vilmorin and Cazaubon, *ibid.*, 1922, **175**, 50.

## CRYSTALLOGRAPHY AND MINERALOGY.

THE predominating thought which arises on commencing to write this Report, on the 27th of December in the year 1922, is that this day is the centenary of the birth of Louis Pasteur at Dôle, the picturesque little French town between Dijon and Pontarlier so familiar to travellers to Switzerland; and that the most interesting crystallographic research carried out during the year and actually communicated to the Royal Society this very month has been the elucidation by means of X-rays of the structure of the crystals of tartaric acid, and the confirmation in all essential details of the classical results of Pasteur's first research, carried out in the year 1848. The propriety of this happy coincidence, and the completeness of the proof of the accuracy of this crystallographic work of Pasteur, will, indeed, go down to posterity as one of the most romantic events in the history of the science. It reminds us very forcibly that the great French savant was a skilled crystallographer first, and a benefactor of the human race by his wonderful bacteriological successes afterwards.

### *Molecules in the Crystalline Condition.*

In last year's Report the writer uttered a protest against the very premature statements which had been made by certain authors, shortly after the announcement of the first results of X-ray analyses of simple binary compounds and elementary substances, that chemical molecules do not exist in the crystalline condition. The writer's own researches had indicated exactly the contrary, and that in most cases of chemical compounds the crystal unit, the similar repetition of which built up the crystal and the representative point of which formed by its repetition in space the space-lattice, was composed of two to four or other small number of chemical molecules; and that within this polymolecular crystal unit, the grosser unit of the crystal structure and the unit cell of the space-lattice, the two, four, or other small number of molecules were mutually arranged in such a manner that the atoms composing them were situated so as to make up one of the 230 types of homogeneous structure which alone are possible to crystals. Although in very simple cases such as those of rock salt, NaCl, and zinc blende, ZnS, the type of structure is so very simple that molecules may not be

definitely identifiable, they are there all the same, for they enter as such from the mother-liquor on crystallisation, and they are again recoverable on solution in a solvent or on fusion to the liquid state. In more complicated cases of substances composed of many atoms it was inconceivable that the molecules were destroyed, on entering the crystal to assist in building up the solid edifice.

The important work of Sir William Bragg on the structure of naphthalene and its derivatives and anthracene, the results of the X-ray analysis of which were fully described in the last Report, gave the first experimental X-ray evidence of the truth of the writer's views as above expressed. For it was conclusively proved that the chemical molecules of these many-atomed organic substances entered into the crystals intact, that the crystal-units of naphthalene and anthracene are each composed of two molecules, and that those of acenaphthene,  $\alpha$ -naphthol, and  $\beta$ -naphthol each contain four molecules.

It was further shown that when a crystal forms in a liquid, or by sublimation, each molecule which takes part in forming the crystal is fixed by the attachment of certain very definite points on its own structure to certain equally specific points on the structure of another molecule, the precision of the adjustment being beautifully exact, indicating very definite form on the part of the molecule, and that the forces exerted have very short ranges. In the case of naphthalene, for instance, the molecules arrange themselves alongside each other, and so that the  $\alpha$ -hydrogens of each molecule seek to attach themselves to the carbon atoms of the neighbouring molecules. The two molecules thus enter the crystal unit in each case intact, and the similar repetition of this polymolecular unit, as the unit cells of a particular space-lattice, forms the crystal. For the molecules become locked into the crystal structure when attachments are made at sufficient points, the whole structure being then as definite and stable as the most perfect engineering structure.

Further work during the year 1922 has united in offering additional confirmation of these now indisputable facts, and it was admirably summarised, and new results referred to, in the lecture which was delivered to the Chemical Society on October 26th by Sir William Bragg.<sup>1</sup> Moreover, a definite law has been advanced by one of his collaborators, Mr. G. Shearer,<sup>2</sup> as expressing the results of investigations carried out at University College, London, to which further reference will be made later in this Report.

Sir William Bragg began his lecture with the recognition of the fact that "every crystal is built up by the repetition throughout

<sup>1</sup> Sir W. H. Bragg, *T.*, 1922, **121**, 2766.

<sup>2</sup> G. Shearer, *Proc. Physical Soc.*, 1922.

its volume of a certain unit," that "the repetition is exact in every detail, so that each unit is a perfect epitome of the whole." In fact he adopts as correct the statement of Barlow<sup>3</sup> that "a homogeneous structure is one, every point within which, if we regard the structure as without boundaries, has corresponding to it an infinitude of other points whose situations in the structure are precisely similar." Having adopted the conception of the unit cell, Sir William agrees to call it the "crystal unit." R. W. G. Wyckoff<sup>4</sup> has come to a somewhat similar conclusion, but has, unfortunately, given the name "crystal molecule" to this unit polymolecular cell, which is to be deprecated as confusing, for crystal molecule is better left to express a chemical molecule as found in the crystal. Sir William then showed that there is no reason to suppose that, in general, the crystal unit is the chemical molecule, but that there is every reason to expect the contrary. The properties of the molecule are those of the substance in the liquid or gaseous state, whereas the solid substance possesses a large number of properties which the liquid substance does not possess. There may be cases where the molecule is the crystal unit (some will be subsequently referred to), but in general this is not so, and Sir William instanced silicon dioxide,  $\text{SiO}_2$ , the chemical molecule of which is incapable, by itself, of producing the rotation of the plane of polarisation of light, which is so characteristic a property of quartz, the crystallised dioxide, which X-ray analysis has shown to consist of crystal units made up each of the substance of three molecules of  $\text{SiO}_2$ .

Further, it does not follow that the molecule exists in the crystal in exactly the same form and condition as in the liquid or gas; the disposition of the constituent atoms may be different (strained or distorted), although in most cases the difference is but slight and certainly not constitutional. For instance, in naphthalene each of the two molecules  $\text{C}_{10}\text{H}_8$  probably resembles very closely in shape the molecule in the liquid state. Still further, X-ray analysis has shown clearly that the crystal unit nearly always contains the substance of more than one molecule, usually two, three, or four. It has also very clearly indicated that the atoms in the unit can be divided into groups, each containing the substance of one molecule.

In the case of organic crystals it has proved to be a very clear division into molecules. But in such simple cases as rocksalt and diamond it is very faint or even indistinguishable. For instance,

<sup>3</sup> W. Barlow, *Min. Mag.*, 1895, **11**, 119.

<sup>4</sup> R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Inst. Washington, Publ. No. 318, p. 43.

the four molecules of NaCl constituting the crystal unit of rock-salt have apparently become indistinguishable. Yet there are some indications "of association of a sodium atom at the edge of the cube with a chlorine atom lying along the diagonal axis through the sodium. Indeed, in sylvine, KCl, this trace of association is sufficient to affect the form of the crystal, giving it the drop in symmetry which it actually shows" (Sir William Bragg in a communication to the writer just received).

With every word of the above, crystallographers can heartily agree, and will be grateful to Sir William Bragg for having so thoroughly cleared the air, and removed the gross misconception which had arisen, according to which crystals were to be regarded in all cases as merely assemblages of "ions," which were confused with those of the electrolytic dissociation hypothesis.

The sense in which "ionisation" is to be understood in connexion with crystal structure was explained in the last Report (pages 220 and 221). It relates only to that one of the two types of chemical combination which is characterised by "electrovalency" (Langmuir), the transference of an electron or electrons from an electro-positive atom, having an excess for inert gas stability, to an electro-negative atom deficient in electrons. The other type of combination is characterised by "co-valency," electrons being shared by two electronegative atoms to make up their common deficiency; the atoms are bound more closely together by this co-valent type of combination. Even in the case of electrovalent combination, however, where it is due to electrostatic attraction owing to the two atoms being left oppositely electrified by the transfer, it has been shown that evidence has been found by Sir William Bragg, notably in the case of potassium chloride, that the molecules formed retain their identity in the crystal structure. In the case of co-valency combination, the molecules are obviously very clearly identifiable.

Sir William recalled that the form of the crystal unit is precisely defined in absolute measure by X-ray analysis, and is necessarily a parallelepiped, the unit cell of the space-lattice, bounded by three pairs of parallel faces, the distance between a pair, now known as the "spacing" of the plane parallel to the pair, being determined by the now famous expression:  $\lambda = 2d \cdot \sin \theta$ , where  $\lambda$  is the wavelength of the X-rays used,  $d$  is the spacing, and  $\theta$  is the smallest of the glancing angles which the incident X-rays must make with the plane in order that reflection may occur. When the spacing of the three pairs of cell-faces is determined, the volume of the unit cell can, of course, at once be calculated. Moreover, the weight of the cell contents is found by multiplying by the density, and the

number of molecules in the unit cell is found by dividing this weight by the weight of the molecule.

The shape of the unit has infinite possibilities, for the corners are all alike in Barlow's sense, that from each of them the outlook is the same; it is these corners, with all the similar points throughout the crystal, which make up the space-lattice. It comes to the same thing as regarding the centres of the cells (or any other identically chosen representative point) as the points of the space-lattice.

A wide field of research now opens out, the determination of the physical constants of this polymolecular crystal unit, inasmuch as it possesses all the properties of the crystal. Its elastic, electric, optical, and thermal, indeed all vectorial, properties and constants now become of immense importance, and all of them will be intimately connected with the detailed internal structure of the crystal unit, that is, with the positions of the atoms composing it, and not improbably with the distribution of the electrons on the atoms. This detailed structure we can look to *X*-ray analysis to afford us. It has to be remembered, however, that *X*-rays cannot distinguish between the two sides of a set of reflecting planes. For instance, in zinc blende the two ends of the polar crystal cannot be discriminated, although the distance between the alternating planes, say those parallel to (111), of zinc and sulphur is three times as great going from zinc to sulphur one way as it is when going the other way. For the intensities of the different orders of *X*-ray spectra reflected depend on the relative magnitude of the spacings and not on their order. Similarly, *X*-rays cannot discriminate between a right-handed spiral and a left-handed one, for the one is the reflection of the other.

The number of chemical molecules in the cell (crystal unit) turns out to be intimately connected both with the symmetry of the crystal and with that of the molecule. For instance, while naphthalene has two molecules in the crystal unit,  $\alpha$ -naphthol, in which a hydroxyl group is substituted for one of the hydrogen atoms of naphthalene and which must therefore be less symmetrical, has four molecules to the crystal unit, the symmetry remaining monoclinic prismatic (holohedral). Similarly, while two molecules of benzene go to the crystal unit of benzene, four molecules are present in the crystal unit of benzoic acid, the molecule of which is obviously more unsymmetrical, and in this case the symmetry is also lower. The symmetry of the crystal thus increases with the number of molecules in the crystal unit, and also with the symmetry of the molecule itself.

The paper of Mr. G. Shearer,<sup>2</sup> already mentioned, was read to the

<sup>2</sup> G. Shearer, *Proc. Physical Soc.*, 1922.

Physical Society on December 8th, 1922, and the writer is able to give some account of it, as he has been most kindly permitted to see the proof-sheets. It discusses very fully the number of asymmetric molecules necessary *per* crystal unit to produce the symmetry of the 32 classes of crystals. The existence of fewer than this number of molecules in the crystal unit is shown to imply symmetry in the molecule itself. The relative positions of the variously orientated molecules in the lattice are also considered, and it is shown that only certain positions are possible. Further, it is concluded that the number of molecules in the elementary cell of the space-lattice is always the minimum necessary to satisfy the symmetry conditions, and that any symmetry of the molecule is reproduced in the crystal. Hence, the crystal always shows at least as much symmetry as the molecules which form it; indeed, in general, the symmetry of the crystal is higher than that of the molecule. Shearer's conclusions are then embodied in the following two rules: (1) The number obtained by dividing the weight of the crystal unit by the molecular weight is either equal to the symmetry number (the number of asymmetric molecules in the unit) or is a sub-multiple of it. (2) In the latter case, the number obtained by dividing the symmetry number by the number of molecules is the symmetry number of the molecule.

Shearer's first rule emphasises the fact that the chemical molecule is the basis of construction of the crystal unit, and thus lays still further stress on the persistence of the molecule in the solid crystalline condition. No case has yet been observed in which the number of molecules is greater than the symmetry number, but cases where it is smaller are common. For instance, the great majority of organic substances examined by X-rays crystallise in the prismatic (holohedral) class of the monoclinic system, their symmetry number is four, and four molecules are found in the crystal unit cell. This obviously corresponds to molecules having no symmetry, which is very general for organic compounds.

The work of Sir William Bragg and his collaborators has shown conclusively that it is possible to obtain decisive evidence of the position of the individual molecules in a polymolecular crystal unit, and also of the positions of the various atoms making up each molecule.

Taking this in conjunction with the rules of Shearer, it is now further possible to obtain a clue to the symmetry of the molecule itself. Sir William has laid down two definite principles concerning the positions of the molecules in the unit. (a) If a crystal unit contain two molecules, one of which is the reflection of the other across a plane of symmetry, and each corner of the unit be occupied by a representative of one of the two types of



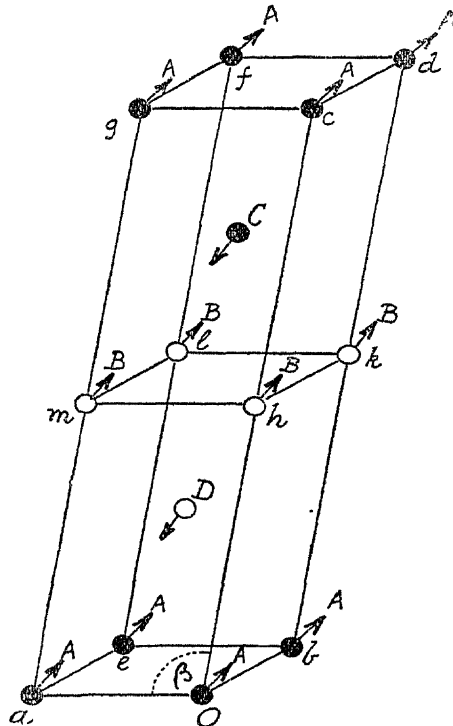
molecule, then the molecule of the other type must lie on a line perpendicular to the plane of reflection, and passing through the centre of one of the cell faces. (b) If a crystal unit contain two molecules, one of which can be brought to coincidence with the other by a digonal axial rotation (the crystal then possessing a plane of symmetry perpendicular to the axis), and if the crystal unit be so

placed that each of its corners is occupied by one of the two types of molecule, then the molecules of the other type must lie on planes perpendicular to the axis and passing through a face-centre.

Now the "spacing" is the distance between any plane and the nearest parallel plane which is identical with the former as regards its relation to the crystal structure. And if there are four molecules in the unit, all four are, in general, differently related to any plane in the crystal. If, for example, the digonal molecules of case (b) lie in planes interleaving the planes of the other molecules, the spacing is halved (that of (010) for instance); this occurs in naphthalene and benzoic acid. If, on the other hand, the digonal molecules lie in the same planes as the original molecules, the spacing is not altered, and this occurs in the two naphthols. Thus by the

halving or otherwise of the spacing the positions of the constituent molecules of a crystal unit can be clearly ascertained. For instance, the positions of the four molecules *A*, *B*, *C*, *D*, of benzoic acid,  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$ , are shown in Fig. 1. The spacings were determinable with great accuracy, as very strong reflections of the X-rays were obtained. The presence of double layers parallel to the (001) plane, and parallel to the very perfect cleavage, is also clearly shown, and the flakiness of benzoic acid crystals is explained by

FIG. 1.



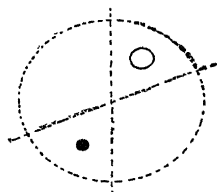
$$Oa = 5.44; Ob = 5.18; Oc = 21.6; \\ \beta = 97^\circ 5'.$$

Crystal Unit Cell of Benzoic Acid.

the much closer packing of the molecules along this plane than along the other principal planes.

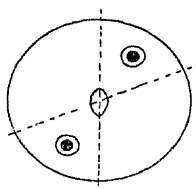
As regards the kind of conclusions to be drawn concerning the symmetry of the molecule itself, when the number of molecules in the crystal unit is less than the symmetry number, the case of naphthalene may again be considered as an example. The symmetry number is four, but there are only two molecules to the crystal unit; hence, the symmetry number of the molecule is two, that is, it possesses twofold symmetry and no more. This is strictly demonstrable only for the crystal molecule (the chemical molecule as it exists in the crystal), yet there must be some character in the substance which disposes its molecule  $C_{10}H_8$  to take up one or other of the two mutually digonal forms according to the circumstances in which it finds itself. Moreover, the X-ray results prove that the molecule of naphthalene must have either a plane of symmetry,

FIG. 2.



The Molecule.

FIG. 3.



The Crystal Unit.

The Symmetry of Naphthalene.

a centre of symmetry, or a digonal axis. The evidence at the time of Sir William's lecture was insufficient to decide which of the three alternatives is correct, but the balance of evidence favoured the centre of symmetry, the *B* molecule being both the reflection and the digonal complement of the *A* molecule, as illustrated by Figs. 2 and 3, the former representing the symmetry of the molecule and the latter that of the crystal unit (monoclinic prismatic).

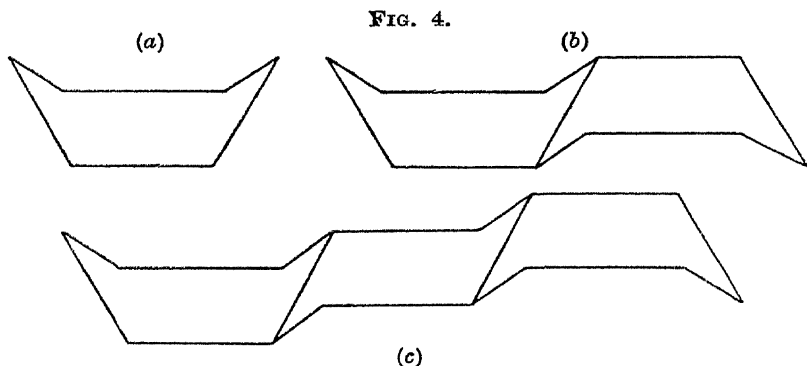
In the private communication to the writer already referred to, Sir William states that he has cleared up the doubt, and that the spacing thought at first to be a full one is really halved, and that there is no doubt whatever that the crystal molecule of naphthalene has a centre of symmetry.

In this letter to the writer Sir William Bragg also makes a further statement regarding anthracene, which is important as it opens up a new method, by use of X-rays, of determining the density of crystallised substances. He has redetermined the spacings with some excellent little crystals provided by Dr. Brady, and these

much more accurate measurements show that the *c*-axis is exactly 2.5 longer than in the case of naphthalene, just the right amount to correspond to an extra ring. The new numbers are :  $a = 8.58$ ;  $b = 6.02$ ;  $c = 11.18$ ;  $\beta = 125^{\circ} 0'$ .

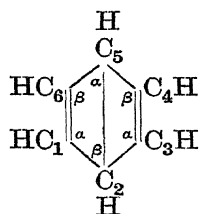
The *b*-axis of naphthalene was found to be 5.98, practically identical with that of anthracene. On working out the density of anthracene from this new information it is found to be 1.255, and this is probably much nearer the truth than the very approximate value, 1.15, given in physical tables. Sir William considers that as the X-ray methods give the actual (absolute) dimensions of the crystal structure they afford a means of determining the density free from errors of inclusions of various sorts.

Some additional X-ray data concerning benzene itself were given in his lecture by Sir William Bragg. The symmetry number of the



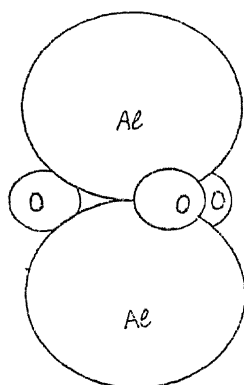
Diagrammatic Forms of (a) Benzene, (b) Naphthalene, (c) Anthracene Molecules.

crystal is eight, as it belongs to the rhombic bipyramidal (holohedral) class, but there are only two molecules contained in the crystal unit. Each molecule possesses, therefore, fourfold symmetry. But it has neither a trigonal nor a hexagonal axis, and therefore the conventional method of representing the molecule as a hexagon is not in accordance with fact. The correct arrangement is slightly different from the sixfold arrangement of carbon atoms in the diamond, and it is shown in perspective in Fig. 4, which also shows at (b) the arrangement in naphthalene and at (c) that in anthracene. The figure of benzene at (a) has the correct amount of symmetry for the molecule of benzene as it occurs in the crystal; it is more in accordance with the Dewar or Ladenburg formula than with that of Kekulé or of Claus. It will be remembered that the formula of Dewar is that here shown, the suffix after the C representing the order of the carbon atom and not the number of atoms.



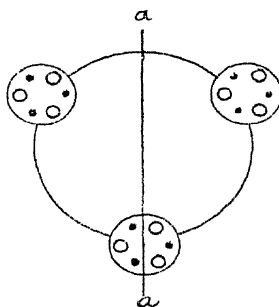
It probably possesses a plane of symmetry and an axis of symmetry perpendicular to it, but this is not trigonal. The figure for the two-ringed molecule of naphthalene at (b) has a centre of symmetry only, which has just been shown to be the fact. That at (c) for anthracene has a third ring of the diamond form inserted between

FIG. 5.



The Crystal Molecule of  $\text{Al}_2\text{O}_3$ ,  
showing arrangement of Atoms.

FIG. 6.



Section through Centre of  
Molecule, showing arrange-  
ment of Electrons in the  
Oxygen Atoms.

those of naphthalene. The sides of all the hexagons are equal, but do not lie in a plane, and the angle between any pair of adjacent sides is the tetrahedral angle  $109^\circ 28'$ .

As a couple of final examples of the truth of Shearer's rules, the simpler inorganic cases of quartz and corundum may be referred to. The quartz crystal is of sixfold symmetry, and as its crystal unit contains three molecules of  $\text{SiO}_2$ , spirally arranged in accordance with trigonal (class 18) symmetry, each molecule has twofold symmetry only. The crystal possesses digonal axes, hence the molecule of  $\text{SiO}_2$  has digonal symmetry. Corundum has twelvefold (trigonal class 21) symmetry, with a crystal unit comprising two molecules of  $\text{Al}_2\text{O}_3$ , the axial ratio being  $a:c = 1:2.73$  and not  $1:1.365$  as usually given. The molecule, therefore, possesses sixfold sym-

metry. X-Ray determinations with the ruby indicate the structure shown in Fig. 5, which agrees with trigonal symmetry, but does not show the nature of the additional twofold symmetry. In Fig. 6, which shows a section of the molecule, the digonal axis is, however, clearly visible at *aa*. Thus the molecule contributes the trigonal and digonal axes, while the crystal structure contributes the planes of symmetry which are characteristic of class 21, for the molecule itself has no plane of symmetry. Sir William Bragg and Mr. Shearer both suggest that, as indicated in Fig. 6, the distribution of the six electrons in the outer shell of the oxygen atoms is such as determines that the crystal shall have the three symmetry planes, in addition to the symmetry elements already present in the molecule owing to the positions of the atoms.

There has thus been accumulated a mass of evidence that the rules enunciated by Shearer are truly valid. The case of tartaric acid is another contributing weighty evidence in the same direction, but this is an altogether remarkable and exceptionally interesting case and will be dealt with in a separate section. Before passing to this, however, reference may be made to an important question raised by Shearer: What determines the choice by any substance of the peculiar form characteristic of itself? For if the molecule be asymmetric all the 32 classes are open to it to crystallise in. But it is very improbable that it will choose the class 32 of highest cubic symmetry, for 48 molecules would then be required to form the crystal unit, whereas 8 molecules is about the maximum number yet found in any space-lattice cell, and this is very exceptional. Asymmetric molecules will therefore crystallise in classes of low symmetry, which is, indeed, found to be the case. Out of a thousand organic aromatic compounds passed in review 60 per cent. require only four molecules to the crystal unit. If, however, the molecule possess some symmetry, its choice will fall on a higher class of symmetry, the higher the greater the symmetry of the molecule.

#### *The Structure of Tartaric Acid.*

The coincidence is a most happy one, that the structure of tartaric acid has been successfully determined by Mr. W. T. Astbury,<sup>5</sup> in Sir William Bragg's laboratory, at the very time of the Pasteur centenary.

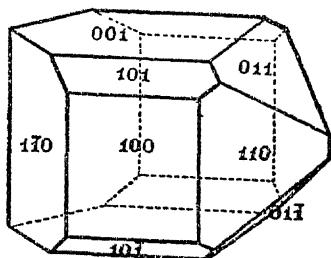
In the paper read to the Royal Society on December 7th, 1922, presenting the results of the X-ray spectrometric analysis, not only are the conclusions of Pasteur confirmed in absolute measure, but some of the more obscure of the properties of this exceptionally interesting and important substance are cleared up by the nature of

<sup>5</sup> *Proc. Roy. Soc.*, 1922, [4].

the structure which is revealed. The crystal structure of ordinary tartaric acid proves to exhibit just such a spiral arrangement of the four carbon atoms of the molecule as was assumed from the crystallographic, enantiomorphous, character of the crystals and from their dextrorotatory power. The theory of stereoisomerism of Le Bel and van't Hoff is in its essentials confirmed, and the direct link between the crystallographic enantiomorphs and the chemical stereoisomerides is revealed. But it is shown to be impossible to distinguish between the dextro- and lævo-forms of such an optically active enantiomorphous substance. The structure established, however, affords a simple explanation of the anomalous rotatory dispersion, involving a maximum for a specific wave-length of light, which is exhibited both by tartaric acid and by its derivatives.

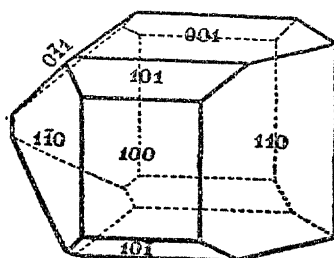
The Bragg ionisation-spectrometer and a Coolidge bulb with molybdenum anticathode were employed, the crystals used being

FIG. 7.



dextro-Tartaric Acid.

FIG. 8.



lævo-Tartaric Acid.

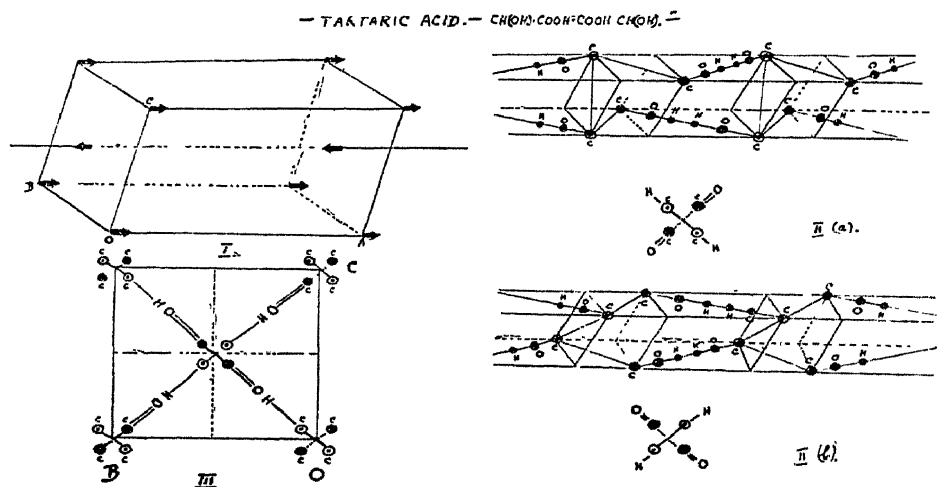
those of ordinary (dextro) tartaric acid,  $C_4H_6O_6$ . The crystals belong to the sphenoidal class 4 of the monoclinic system, and their constants are  $a : b : c = 1.2747 : 1 : 1.0266$ ;  $\beta = 100^\circ 17'$ ; density 1.759. The next two figures (Figs. 7 and 8) represent two typical crystals of the dextro- and lævo-varieties of tartaric acid, which differ essentially by the dextro-crystal exhibiting only the right clino-prism  $\{011\}$  and the lævo-crystal only the left clino-prism  $\{01\bar{1}\}$ .

The crystal unit is found to contain two molecules  $C_4H_6O_6$ , and as the symmetry number is two, each molecule must be asymmetric in accordance with Shearer's rule, and with the absolutely essential condition for optical activity, the absence of second-order symmetry elements, symmetry planes being certainly absent. The crystal also being likewise optically active, must be without any plane of symmetry, and must possess some kind of spiral structure, which is right-handed in one of the active varieties and left-handed in the other.

The structure which Mr. Astbury eventually deduces from his

X-ray spectrometric measurements of spacings and intensities of the various spectral orders, together with the known crystallographic and density data above given, is shown in Fig. 9. The portion of the figure marked I shows the crystal unit of tartaric acid and the arrangement of the molecules. Of the two molecules forming each crystal unit one is the digonal complement of the other, and the spacing of the (010) planes is found to be halved in consequence. Moreover, the structure exhibits not only one spiral but two spirals, differently handed but not mirror-image complements and occurring in different parts of the structure. One is associated with the four carbon atoms at the centre of the molecule

FIG. 9.



The Structure of Tartaric Acid.

and forming its nucleus, and the other with the four hydroxyl groups. To the former spiral is due the optical activity of the solution, for it is permanent, persisting in the molecule itself; whereas the latter spiral appears only in the crystal structure and disappears in solution. Its rotation effect on the plane of polarisation of light is greater than that in the opposite direction due to the first screw, and so determines the sign of rotation of the tartaric acid crystal, which appears to be the opposite of that of the solution.

Parts II(a) and II(b) show the two enantiomorphous forms of the crystal unit, and the arrangement of the two molecules along the axis  $a$ , as well as the projection of the carbon core on a plane perpendicular to axis  $a$ . Part III shows the section of the crystal unit perpendicular to axis  $a$ , with the arrangement of the molecule

at each corner and its digonal complementary molecule at the centre.

This structure agrees with all the purely crystallographic data concerning tartaric acid. The two forms shown at II(a) and II(b) are clearly enantiomorphous with respect to each other. It also explains the one perfect cleavage parallel (100), the plane about which lie the junctions of the hydroxyl groups. For the molecules are held together end to end by forces between the hydrogen atoms of adjacent hydroxyl groups, one OH group being carboxylic and the other alcoholic. None of the strong valency forces acts across this plane (100), but only these weaker forces acting from molecule to molecule and serving to bind them together in the crystal lattice; hence, it is pre-eminently a plane of possible cleavage, as is actually observed. The junctions in the ( $\text{=OH-}$ ) linkages are stronger, hence, there is no cleavage across them, doubtless due to the oxygen having double linkage. The distance between carbon and oxygen atoms in the ( $\text{-C=O}$ ) groups is also less than in the ( $\text{-C-O-H}$ ) groups, and this is doubtless due to electron-sharing.

Another interesting fact is that there is a particularly intense first-order reflection of the X-rays from the (011) plane, and it is precisely this plane which has the greatest density of atoms per unit area; the interleaving also throws most of the energy into the first-order spectrum from this plane. Now the crystals themselves usually develop these planes characteristically, (011) on right-handed crystals and (0 $\bar{1}$ 1) on left-handed ones, as shown in Figs. 7 and 8. This agrees with the well-known crystallographic principle that a crystal tends to develop best the planes of greatest reticular density.

The spiral nature of the two enantiomorphous structures shown at II(a) and II(b) will be obvious, and the fact that they are of opposite winding. The four carbon atoms which form the nucleus of the molecule are situated at alternate corners of the oblique parallelepiped, and this automatically produces an irregular spiral formation within the molecule itself. Moreover, the hydroxyl groups are arranged in another spiral of opposite kind, the junction between the hydrogen atoms being only possible when this is so, this second twist reversing, and more, the twist of the nucleus of the molecule just described. Each of these twists in one enantiomorph is the opposite of that in the other, and this reversal of twist inverts the order of succession of the ( $\text{-H}$ ), ( $\text{-OH}$ ), and ( $\text{-CO}\cdot\text{OH}$ ) groups round the asymmetric carbon atoms.

The structure agrees with the fact that the plane of the optic axes of tartaric acid is perpendicular to the one symmetry plane of the monoclinic crystal, the obtuse bisectrix coinciding with the



unique digonal symmetry axis  $b$ , so that the two optic axes make equal angles with axis  $b$ ; it consequently also agrees with the fact that the rotatory power along each of the two optic axes is the same, namely, according to Dufet  $8^{\circ} 33'$  per millimetre of thickness of plate for red lithium light, increasing with shortening wave-length to  $14^{\circ} 14'$  for green thallium light.

The unusual property was discovered by Biot, that solutions of tartaric acid in water or alcohol show a maximum rotation in the green, and also that the specific rotation of an aqueous solution at a given temperature is a linear function of the concentration:  $[\alpha] = A + B\epsilon$ , where  $\epsilon$  is the proportion of water in the solution. By extrapolation he also obtained the rotation of the anhydrous acid, and predicted that for red light this would change sign at  $23^{\circ}$ . This prediction was subsequently verified. Now these remarkable facts are also explained by the structure of the crystals as now revealed by X-rays, the two opposite rotatory systems produced by the two opposite spiral twists of the two parts of each molecule being adequate to account for them completely. The involved explanation suggested by Lowry is thus unnecessary, the structure alone affording a sufficient cause.

The final conclusion is that the dextrorotatory power of ordinary tartaric acid is to be ascribed solely to the presence within the molecule of a system of four carbon atoms forming an irregular spiral. The direction of twist of this spiral is the opposite of what it is in *lævo*-tartaric acid. Arguing from the analogy of Reusch's pile of mica plates simulating quartz and its rotation, a clockwise spiral of atoms will produce dextrorotation (meaning that the plane of polarisation of light is rotated to the right or to the left from the point of view of a person looking into the microscope), and an anti-clockwise spiral *lævorotation*. In *dextro*-tartaric acid the order of sequence of the  $(-H)$ ,  $(-OH)$ , and  $(-CO\cdot OH)$  groups is anti-clockwise, as we look towards the asymmetric carbon atom in the direction leading towards it from its companion asymmetric carbon atom. The aspect of the molecule as a whole shows a distorted tetrahedral arrangement of bonds.

It would thus appear that the structure arrived at as the result of this interesting investigation explains in a most satisfactory fashion even the smallest details of the physical properties, in many ways peculiar and unusual, of tartaric acid, as well as confirming the general conclusions of Pasteur and later workers as to the essential characters of the two varieties and their relations to the optical activity of this typical enantiomorphous substance, the first of the large class of such substances which have since become known.

*Further Light on Functions of Exterior Electrons.*

It was shown in the last Report that some light had been thrown on the situation of the outer electrons of the atoms by some special experiments, concerning the intensity of certain orders of X-ray reflection from the planes of atoms in the diamond and fluorspar, by Sir W. H. Bragg and Mr. H. Pealing. It is immaterial, as regards the symmetry of the atoms, whether the electrons are stationary or moving in orbits, so long as in the latter case the distribution of the orbits or of their normals is considered. In any case, the outer electrons are prime factors in the problem of atomic symmetry, and the concluding portion of Shearer's paper<sup>2</sup> deals with this aspect of the subject. Now a considerable number of the elements crystallise in the highest class 32 of cubic symmetry, while the crystal unit only contains two or four atoms.

If we consult Shearer's table giving the number of asymmetric molecules required to build up the crystal unit in each of the 32 classes (this number varies from 1 in class 1 to 48 in class 32), and divide the 48 there given as corresponding to class 32 by 2 or 4, we arrive at 24-fold or 12-fold symmetry as being that possessed by these elementary atoms, and this corresponds to one of the lower classes of the cubic system. From this Shearer concludes that there is some form of cubic arrangement of the electrons or their orbits in these atoms. Carbon, in the diamond form, even if considered as only belonging to class 31 (whereas there is more evidence that it really belongs to class 32), as it has eight atoms to the crystal unit, would have the symmetry number three, and would therefore possess a trigonal axis. Hull's structure for graphite also supports the assumption that the carbon atom possesses a trigonal axis of symmetry in its structure. It would thus appear that for crystallographic purposes what matters is the outer electronic arrangement, and not the atomic nucleus.

In the last Report it was also shown that a formula for the intensity of reflection from a crystal plane of atoms had been arrived at by W. L. Bragg, R. W. James, and C. H. Bosanquet, embodying also some important results of C. G. Darwin and A. H. Compton, and also those of P. Debye and P. Scherrer, in which occurred an important factor,  $F$ , which depended on the number and arrangement of the electrons of the diffracting atoms constituting the plane. C. G. Darwin,<sup>6</sup> however, has since shown that on account of the difficulty in determining the effective coefficient of extinction of the X-rays the result afforded by the formula is not quite accurate, and has suggested a new formula, based on his experiments with powdered crystals, as affording more accurately the

<sup>6</sup> C. G. Darwin, *Phil. Mag.*, 1922, [vi], 43, 800; *A.*, ii, 416.

amplitude of the wave scattered by all the electrons in a single atom in the direction of the reflected beam. A. H. Compton and N. L. Freeman <sup>7</sup> have also arrived at the same conclusion, and have made quantitative measurements of the intensity of X-rays derived by reflection from rocksalt and then scattered by powdered crystals of sodium chloride, using the  $K_{\alpha}$  line from molybdenum ( $\lambda = 0.708$  Å.U.). They found that the theory of X-ray reflection which has been put forward by Sir W. H. Bragg then gives accurate results. In a further paper, W. L. Bragg, James, and Bosanquet <sup>8</sup> revise their results in the light of these contemporary researches, and have reduced the error due to the extinction uncertainty to a minimum. The results then indicate that neither in the sodium nor the chlorine atom can there be eight electrons in an outer shell, or eight electrons describing orbits lying on an outer sphere; but that a combination of circular and elliptic orbits would agree with the  $F$  curves as now corrected. This would appear to indicate that the theories of Bohr and of Langmuir concerning atomic structure are neither alone correct, and that the truth lies somewhere between the two, a conclusion which has lately been emphasised from all sides.

*Effect of Temperature on X-Ray Reflection.*

This has been studied during the year by I. Backhurst <sup>9</sup> in Sir W. H. Bragg's laboratory. According to C. G. Darwin and to P. Debye the intensity diminishes as the temperature of the crystal increases, and it does so more rapidly as the angle of reflection increases. These conclusions were supported by experiments made some time ago by Sir William Bragg, and are now fully confirmed by Mr. Backhurst's results.<sup>9</sup> Sir W. H. Bragg's apparatus was used, the crystal being placed in an electric heater furnished with mica windows for ingress and egress of the X-rays, the thermometer bulb being immediately over the crystal. Sir W. H. Bragg's original apparatus only permitted of determinations with rocksalt and sylvine up to  $370^{\circ}$  and  $311^{\circ}$ , respectively, but in the new arrangement a much higher temperature can be maintained, and the crystal be environed by an atmosphere of nitrogen, a thermocouple being substituted for the thermometer at the higher temperatures. Crystals of aluminium, carborundum, graphite, diamond, sapphire, and ruby were studied. Aluminium showed a very marked decrease of reflection intensity with rise of temperature, in fair agreement with Debye's theory. Carborundum proved stable enough to be tested (using a special furnace) up to as high a tempera-

<sup>7</sup> A. H. Compton and N. L. Freeman, *Nature*, 1922, **110**, 38.

<sup>8</sup> W. L. Bragg, R. W. James, and C. H. Bosanquet, *Phil. Mag.*, 1922, [vi], **44**: 433; A., ii, 703.

<sup>9</sup> I. Backhurst, *Proc. Roy. Soc.*, 1922, [A], **102**, 340.

ture as  $960^{\circ}$ , and gave much greater decreases of intensity for the higher spectral orders. Graphite, studied up to  $850^{\circ}$ , agreed with theory, but also showed an unusually high coefficient of expansion perpendicular to (0001), which further emphasises the weakness of the bonds in this direction referred to in the last report. Diamond was remarkable as showing practically no decrease of intensity, owing to its great strength and the slight degree of thermal agitation which it evinces. Ruby and sapphire showed an anomalous effect, indicating that the pair of aluminium atoms remain in contact and do not share in the expansion of the lattice which is observed.

*Crystal Structure as determined by X-Rays and the 230 Space-groups.*

A fact which has become more and more emphasised during the year is that all the results of X-ray analysis of crystals which are open to no ambiguity have shown that the crystal structure conforms to one or other of the 230 types of homogeneous structure which Schoenflies, Fedorov, and Barlow united in specifying as those alone possible to crystals. The facts are concisely expressed as follows: "Direct experimental proof is afforded that the structural units, the component chemical atoms and their molecular or polymolecular groups, are arranged in crystals in one or other of the 14 space-lattices as regards the main grosser structure (that of points representative of the molecule or small group of molecules), and in one or other of the 230 point-systems as regards the ultimate units, the chemical atoms themselves. . . . Indeed, it must happen that the structure revealed by X-rays shall agree with one of the 230 types of homogeneous structures which alone are possible to crystals." These words, quoted from the second edition of the writer's book<sup>10</sup> published early in the year, page 705 of Vol. I, are thus now by the year's work more than ever confirmed.

It is consequently of the highest importance for workers in the X-ray field of research to have before them a clear presentment of the 230 types. They are only in the simpler cases hard-and-fast stereotypes; for the great majority permit of considerable variety in the details of the arrangement of the ultimate units (atoms), and it is the quite feasible task of the X-ray investigation to discover these details. The 65 (of the 230) more fundamental point-systems of Sohncke, to which or to their special cases most of the structures yet elucidated correspond (some of these special cases being simple space-lattices themselves), involve only coincidence movements or symmetry elements of the first order (rotations about axes, possibly screw axes, and translations), the other more rarely natur-

<sup>10</sup> A. E. H. Tutton, "Crystallography and Practical Crystal Measurement." Second edition in two volumes, Macmillan & Co., 1922.

ally occurring 165 types involving also operations and symmetry elements of the second order (symmetry planes, mirror-image-reflection planes, mirror-axes, inversions, or symmetry centres). The 65 Sohncke point-systems are all described and illustrated, with exact reproductions of Sohncke's drawings, in the writer's book just referred to, pages 601 to 621. The special cases are also described in which the point-system becomes reduced directly to one of the 14 space-lattices of Bravais, and the derivation of the other 165 point-systems from the 65 is traced, and a table given showing the distribution of the whole 230 among the 32 crystal classes and seven crystal systems, with the Schoenflies class symbols and his space-group numbers. The details of the symmetry of all the 230 space-groups have been given by all three of the original independent discoverers, but the notation of Schoenflies, as given in his "Krystallsysteme und Krystallstruktur," published in Leipzig in 1891, has become more generally adopted. An excellent summary of it is given by H. Hilton in his "Mathematical Crystallography," published in Oxford in 1903. P. Niggli has more recently, in his "Geometrische Krystallographie des Discontinuums" (Leipzig, 1919), given a considerable number of special cases of the space-groups, and has specified the positions within the unit cell of each space-group of all its symmetry elements.

H. Hilton, in a paper <sup>11</sup> to the Mineralogical Society in June last, refers to the bewildering variety of other suggested notations than that of Schoenflies, and points out that the Schoenflies notation itself suffers from two serious drawbacks. The first is that rotation and rotatory reflection are taken as fundamental operations, whereas for crystal-structure purposes rotation and rotatory inversion are needed. The second is that it is troublesome and expensive to print, involving small index and suffix numbers or letters after the capital letter symbol. He therefore suggests yet another notation, involving only English type and nothing above or below the line.

In October last a memoir of 180 pages in book form by R. W. G. Wyckoff <sup>4</sup> was published by the Carnegie Institute of Washington, in which all the special cases of the space-groups have been worked out. The matter contained is largely tabular, giving the co-ordinates of the most generally placed equivalent points and all the special cases of these equivalent points, contained within the unit of structure of each of the 230 space-groups. In this form the information will be immediately available to X-ray analysts. For a review of all the X-ray analyses yet carried out has shown that the number of particles (atoms) contained in the unit cell is

<sup>11</sup> H. Hilton, *Min. Mag.*, 1922, **19**, 319.

usually smaller than the number of most generally placed equivalent points of the space-group having the symmetry of the crystal. The special arrangements of the equivalent points (on axes, planes, or other symmetry elements), whereby the number of symmetry elements is reduced, are thus of great importance to the X-ray analyst. This book is, therefore, one of very considerable value. Reference has, however, been already made to one point which it would be a clear advantage to remedy in any future edition of the work, namely, the replacement of the term "crystal molecule" by "crystal unit," which is really what Wyckoff means by the term. As Sir William Bragg remarks in a letter to the writer, the term "crystal molecule" is much better left to indicate the chemical molecule as it exists in the crystal unit, which latter is usually, as already so clearly proved, composed of more than one chemical molecule. For it is, indeed, most essential to discriminate between three very different things, the crystal unit, the crystal molecule, and the chemical molecule. By the latter is to be understood the molecule as it exists in the gaseous or liquid condition.

#### *Miscellaneous X-Ray Results.*

An important paper by M. Siegbahn,<sup>12</sup> on the improvements which he has introduced into X-ray spectrometry, gives some remarkably accurate determinations, suitable for use as *Standards of Reference*, of the angle of reflection of the first-order  $K_{\alpha}$  radiation of copper from calcite. They are as follows:

With crystal face polished.				With rough cleavage face.			
14°	42'	2.8"		14°	42'	0.0"	
14	41	59.8		14	41	59.9	
14	41	59.6		14	41	59.2	
14	42	1.3		14	41	58.0	
14	41	59.5		14	41	59.6	
14	42	2.3		14	42	5.5	
Mean	14°	42'	0.8"	Mean	14°	42'	0.4"

The difference for the two conditions of face being so minute, the final mean  $14^{\circ} 42' 0.6''$  may be taken as a standard value. We have here an excellent proof that it is the inner planes within the crystal substance that are chiefly concerned in contributing to the reflection, and not the surface of the crystal face.

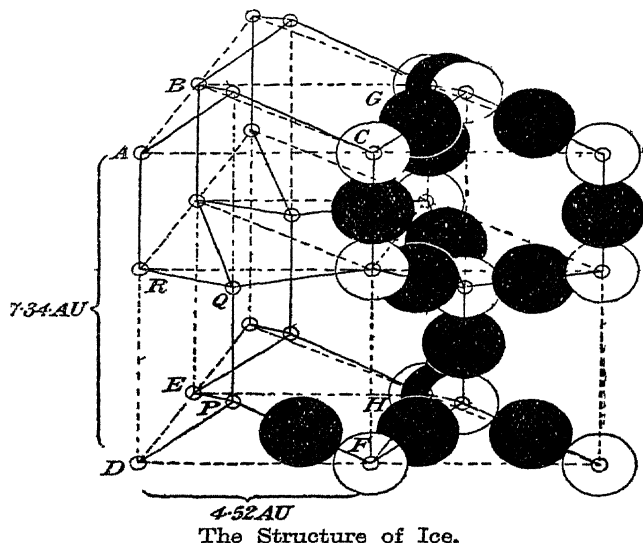
*A Modification of the Powder Method* was described by E. A. Owen and G. D. Preston to the Physical Society on December 8th, 1922, in which plates of aluminium, iron, copper, lead, and magnesium were examined on the Bragg X-ray spectrometer, employing radiation direct from a molybdenum anticathode. Excellent

<sup>12</sup> *Compt. rend.*, 1921, 173, 1350; *A.*, ii, 104.

spectra were obtained, which enabled the structure of these metals to be readily determined. Sir William Bragg pointed out that one of the planes becomes unduly accentuated by the polishing process, and this has to be remembered in interpreting the results.

*The Structure of Ice.*—In the last Report the work of D. M. Dennison was recorded, who found ice to have the structure of a close-packed hexagonal lattice, composed of two sets of interpenetrating triangular prisms, with edges 4.52 and height 7.32 Å.U., the axial ratio being  $a:c = 1:1.62$ . Sir William Bragg,<sup>13</sup> revising this work and the earlier work of A. St. John, finds that four such lattices interpenetrate

FIG. 10.



trate to form the complete structure, and confirms Dennison's figures for the dimensions. Each oxygen atom is at the centre of gravity of four neighbouring equidistant oxygen atoms, from each of which it is separated by a hydrogen atom, there being twice as many hydrogen atoms round each oxygen atom as there are oxygen atoms round each hydrogen atom. The structure is shown in Fig. 10.

The structure is an extremely open one, corresponding to the low density 0.9165, and it is easy to suppose that loose  $\text{H}_2\text{O}$  molecules, liquid water, would occupy less space, so that the expansion on freezing, and the melting of ice by pressure, is accounted for. The dimensions of the hydrogen atom are here measured for the first time, the sum of the diameters of oxygen and hydrogen atoms being 2.76 Å.U. As the diameter of the oxygen atom is 1.30, that of

<sup>13</sup> *Proc. Phys. Soc.*, 1922, 34, 98.

hydrogen will be 1.46 Å.U. This is not too large, for G. Aminoff<sup>14</sup> has calculated it from investigations of magnesium and manganese hydrides as 2.16, and from the structure of ice as 2.24. From its relation to the alkali metals hydrogen might well be expected to have this slightly larger diameter than oxygen.

*Structure of the Crystallised Elements.*—A. W. Hull<sup>15</sup> has published two papers since the last report, regarding further results with his powder method. Summarising, cobalt, nickel, rhodium, palladium, iridium, platinum, and thorium have the face-centred cube structure. Iron has the centred cube structure. Ruthenium and osmium have hexagonal close-packed structures, the axial ratio of each being 1.59. Titanium, zirconium, and cerium have distorted hexagonal close-packed structures, with axial ratios 1.59 in the first two cases and 1.62 in the case of cerium.

L. W. McKeehan<sup>16</sup> has determined the structure of potassium cooled to  $-150^{\circ}$ , and found the atoms to be arranged on a centred-cube lattice, with  $a = 5.20$  Å.U. The observed crystalline structure does not persist as the metal is allowed to regain room temperature. He has also investigated crystallised glucinum and found that it resembles magnesium, zinc, and cadmium (close-packed hexagonal) rather than calcium, strontium, and barium. There are two symmetrically interpenetrating hexagonal space-lattices, the side being 2.283 Å.U.

The crystal structure of germanium has been determined by N. H. Kolkmeier<sup>17</sup> by the powder method, and found to resemble that of diamond, and the similar forms of silicon and tin. The lattice parameter  $a = 5.61$  Å.U.

Iron in its various forms has been studied by A. Westgren and A. E. Lindh,<sup>18</sup> and also by Westgren and G. Phragmen.<sup>19</sup> For pure iron ( $\alpha$ -iron) Hull's result is confirmed, namely, a centred-cube lattice. Between  $800^{\circ}$  and  $836^{\circ}$ , within the  $\beta$ -iron region, the atomic grouping remains the same. They regard allotropy and polymorphism as synonymous, and that  $\beta$ -iron is only a particular modification of  $\alpha$ -iron. Austenite and pure iron at  $1000^{\circ}$  were found to have a face-centred cube lattice, which is also characteristic of  $\gamma$ -iron. Hence the two really different forms are  $\alpha$ - and  $\gamma$ -iron. Martensite was found to be  $\alpha$ -iron, as was also high-speed tool steel

<sup>14</sup> G. Aminoff, *Geol. För. Förh.*, 1921, **43**, 389; *A.*, ii, 496.

<sup>15</sup> A. W. Hull, *Physical Rev.*, 1921, **18**, 88; *J. Franklin Inst.*, 1922, **193**, 189; see also *A.*, ii, 624.

<sup>16</sup> L. W. McKeehan, *Proc. Nat. Acad. Sci.*, 1922, **8**, 254, 270; *A.*, ii, 709.

<sup>17</sup> N. H. Kolkmeier, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 125; *A.*, ii, 713.

<sup>18</sup> A. Westgren and A. E. Lindh, *Z. physikal. Chem.*, 1921, **98**, 181; *A.*, ii, 152.

<sup>19</sup> A. Westgren and G. Phragmen, *ibid.*, 1922, **102**, 1; *A.*, ii, 711.



hardened at 1275°. Iron wire at 800°, 1100°, and 1425°, within the  $\beta$  and  $\gamma$  regions, has the centred-cube structure like  $\alpha$ -iron. The transition which occurs at 900° ( $A_3$ ) is reversed at 1400° ( $A_4$ ). The presence of carbon extends the space-lattices. Cementite and spiegeleisen crystals were found to be identical, of rhombic symmetry with four molecules of  $Fe_3C$  to the crystal unit.

*Lithium Hydride* has been studied by J. M. Bijvoet and A. Karsen,<sup>20</sup> and found to be cubic with four molecules of  $LiH$  to the crystal unit, the side of which is  $a = 4.10$  Å.U., the structure resembling that of rocksalt.

*Silver Oxide*, which crystallises in small octahedra, has been investigated by the powder method by R. W. G. Wyckoff,<sup>21</sup> and found to resemble cuprous oxide, with a unit cube containing two molecules of  $Ag_2O$ , and an edge of 4.768 Å.U.

*Magnesium Oxide* has been reinvestigated by W. Gerlach and O. Pauli<sup>22</sup> by the powder method, and found to be constructed on a face-centred cube lattice, with length of side 4.22 Å.U., identical with the previous value.

*Glucinum Oxide* has been investigated by L. W. McKeehan,<sup>22a</sup> who finds the diffracting centres to lie at the points of two symmetrically interpenetrating hexagonal space-lattices having the side 2.696 Å.U.

*Alkali Halides*.—Ammonium chloride has been studied by R. W. G. Wyckoff<sup>23</sup> by the spectrometric and powder methods (first paper) and by the Laue radiographic method (second paper), and he has decided for tetrahedral and not plagihedral symmetry, the unit cube having only one molecule contained in it. The chlorine atoms are situated at the cube corners, the nitrogen atom at the cube centre, and the four hydrogen atoms are arranged tetrahedrally around and near the nitrogen atom. The side of the unit cube is 3.859 Å.U.

For this work some excellent crystals, clear rectangular prisms several millimetres in size, were obtained, from solutions containing urea. They afforded a refractive index of 1.639, and gave excellent Laue radiograms.

Lithium chloride, bromide, and iodide, and sodium, potassium, rubidium, and caesium fluorides have been investigated by E. Posnjak and R. W. G. Wyckoff,<sup>24</sup> and the results, together with

<sup>20</sup> J. M. Bijvoet and A. Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, 25, 26; *A.*, ii, 569.

<sup>21</sup> R. W. G. Wyckoff, *Amer. J. Sci.*, 1922, [v], 3, 184; *A.*, ii, 291.

<sup>22</sup> W. Gerlach and O. Pauli, *Z. Physik*, 1921, [vii], 2, 116.

<sup>22a</sup> L. W. McKeehan, *Proc. Nat. Acad. Sci.*, 1922, 8, 254, 270; *A.*, ii, 709.

<sup>23</sup> R. W. G. Wyckoff, *Amer. J. Sci.*, 1922, [v], 3, 177; 4, 469; *A.*, ii, 290.

<sup>24</sup> E. Posnjak and R. W. G. Wyckoff, *J. Washington Acad. Sci.*, 1922, 12, 248; *A.*, ii, 499.

those of former work, are tabulated for twenty salts of the type  $RX$ . All prove to be of rocksalt type with simple cubic lattice, except caesium chloride, bromide, and iodide, which possess the centred-cube lattice structure.

In the writer's opinion, this difference of structure on the part of the caesium halides at once explains why a clear progression in crystallographic constants and properties is not manifested by the potassium, rubidium, and caesium salts of halogen acids, similar to that which characterises the sulphates. The caesium halides are obviously not strictly comparable with the corresponding potassium and rubidium halides.

W. P. Davey and Miss F. G. Wick<sup>25</sup> also find caesium chloride to be constructed on a cubic lattice, with caesium atoms at the corners and a chlorine atom at the centre of each cube. The spacings for the cube planes are for  $KCl$  6.26 (Bragg), for  $RbCl$  6.60 (Wyckoff), and for  $CsCl$  4.12 Å.U. (Davey and Wick), the latter body-centred cube value being thus quite different from the values for the former two rocksalt groupings.

*Cuprous Chloride, Bromide, and Iodide* have been studied by R. W. G. Wyckoff<sup>26</sup> and prove to have the zinc blende arrangement of atoms in their crystals, the lengths of the sides of the unit cubes being respectively 5.49, 5.82, and 6.10 Å.U.

*Potassium Cyanide* has been examined by R. M. Bozorth,<sup>27</sup> using all three methods (of Laue, Bragg, and Debye). A structure somewhat similar to that of rocksalt is indicated, with potassium atoms at the sodium positions and the carbon and nitrogen atoms near the chlorine atomic positions, and 1.15 Å.U. apart, equidistant in each case from the chlorine position in rocksalt.

*Cadmium Iodide* has also been examined by Bozorth<sup>27a</sup> and found to be trigonal and not, as supposed, hexagonal. The crystal unit contains one molecule  $CdI_2$ , and the shortest distance between the centres of the cadmium and iodine atoms is 3.00 Å.U., which is exactly the sum of the radii given by W. L. Bragg.

*The Aragonite Group of Minerals* (aragonite, strontianite, witherite, and cerussite) forms the subject of a paper by M. L. Huggins,<sup>28</sup> who suggests that each carbon atom, as in calcite, is linked by double bonds to three oxygen atoms, each oxygen atom to two calcium atoms and one carbon atom, and each calcium atom to six oxygen

<sup>25</sup> W. P. Davey and Miss F. G. Wick, *Physical Rev.*, 1921, **17**, 403.

<sup>26</sup> R. W. G. Wyckoff and E. Posnjak, *J. Amer. Chem. Soc.*, 1922, **44**, 30; *A.*, ii, 295.

<sup>27</sup> R. M. Bozorth, *ibid.*, 317; *A.*, i, 441.

<sup>27a</sup> *Ibid.*, 2232; *A.*, ii, 857.

<sup>28</sup> M. L. Huggins, *Physical Rev.*, 1922, **19**, 354; *A.*, ii, 463.

atoms, at the corners of an irregular octahedron (presumably a rhombic pyramid).

*The Group of Isomorphous Nitrates* of lead, barium, strontium, and calcium,  $R(NO_3)_2$ , crystallising in the tetrahedral pentagonal dodecahedral class 28 of the cubic system, has been studied by L. Vegard<sup>29</sup> by the powder method. The metallic atoms are arranged in a face-centred lattice; three oxygen atoms and one nitrogen atom form a group at four of the corners of a cube, this group having a trigonal axis and being surrounded by four metallic atoms.

*Sodium Chlorate and Bromate*, which also crystallise with class 28 symmetry, have been reinvestigated by R. G. Dickinson and E. A. Goodhue.<sup>30</sup> The atoms appear to be arranged with the symmetry of the Schoenflies space-group  $T^4$ , all the oxygen atoms being equivalent.

*Phosphonium Iodide*,  $PH_4I$ , has been submitted by R. G. Dickinson<sup>31</sup> to both the Bragg and Laue methods of  $X$ -ray analysis, and found to afford a similar structure to ammonium chloride at low temperatures. The unit cell has the dimensions 6.34 by 6.34 and 4.62 Å.U.

*Ammonium Chloroplatinate*,  $(NH_4)_2PtCl_6$ , has been examined by the Laue method by R. W. G. Wyckoff and E. Posnjak,<sup>32</sup> and appears to have a structure resembling that of fluorspar, in which the  $PtCl_6$  groups replace the calcium atoms, and the ammonium groups replace the fluorine atoms. The crystal unit cubic cell has a side of 9.843 Å.U. Curiously enough, Wyckoff<sup>33</sup> also finds that the crystals of the complex nickel ammonia compounds of the type  $NiX_2 \cdot 6NH_3$ , formed when ammonia is added to solutions of nickel chloride, bromide, and iodide respectively, are arranged in a similar manner isomorphous with ammonium chloroplatinate, the sides of the unit cells in the three cases being 10.09, 10.48, and 11.01 Å.U. In each case there are four molecules in the crystal unit cell, the nickel atoms replacing those of platinum, and the nitrogen atoms occupying the positions of the chlorine atoms.

*Potassium Chloroplatinate*,  $K_2[PtCl_6]$ , and the salts  $Rb_2[PdBr_6]$  and  $[Ni(CH_3)_6]Cl_2$  have also been investigated by P. Scherrer and P. Stoll<sup>34</sup> and found to resemble fluorspar and ammonium chloroplatinate, the co-ordinated complex in square brackets replacing the calcium.

<sup>29</sup> L. Vegard, *Z. Physik*, 1922, **9**, 395; *A.*, ii, 503.

<sup>30</sup> R. G. Dickinson and E. A. Goodhue, *J. Amer. Chem. Soc.*, 1921, **43**, 2045; *A.*, ii, 145.

<sup>31</sup> R. G. Dickinson, *ibid.*, 1922, **44**, 1489; *A.*, ii, 640.

<sup>32</sup> R. W. G. Wyckoff and E. Posnjak, *ibid.*, 1921, **43**, 2292; *A.*, ii, 214.

<sup>33</sup> R. W. G. Wyckoff, *ibid.*, 1922, **44**, 1239; *A.*, ii, 573.

<sup>34</sup> P. Scherrer and P. Stoll, *Z. anorg. Chem.*, 1922, **121**, 319; *A.*, ii, 524.

*Ammonium Fluosilicate* has been structurally analysed by X-rays by R. M. Bozorth,<sup>35</sup> and found also to resemble ammonium chloroplatinate, ammonium chlorostannate, and potassium chlorostannate, namely, in possessing the type of structure of fluorspar, the fluorine atoms of the latter being replaced by an ammonium group, and each calcium atom by a fluosilicate group, with the six fluorine atoms equidistant from the silicon atom in the direction of the crystal axis. The unit cube contains four molecules of  $(\text{NH}_4)_2\text{SiF}_6$  and the side measures 8.38 Å.U. The sides of the other three compounds mentioned are respectively 9.84, 10.05, and 9.96 Å.U.

*Silver Molybdate* has been examined by R. W. G. Wyckoff<sup>36</sup> by both the X-ray spectrometric and the radiographic methods, and found to possess a structure like that of magnetite and the spinels, with eight molecules to the unit cube, which has a side of 9.26 Å.U.

*X-Radiograms of Strained Crystals* have been studied by A. F. Joffe and M. V. Kirpicheva.<sup>37</sup> In the case of rocksalt, gradually loaded by means of an electromagnet, when the limit of elasticity is passed the Laue spots elongate, and even before it is reached the spots elongate and break up into stratifications, increasing in number with the strain, due to different small crystals into which the crystal breaks up, each of the same structure as the original crystal. The molecules glide along the plane of the rhombic dodecahedron and also rotate. The method is suitable for determining the limit of elasticity, and the mode of destruction. A method is also described which gives on two photographs the strains in every direction, and enables all the constants of elasticity to be determined from one small crystal.

#### *Crystallographic Chemical Investigations.*

The last two papers of the writer's research on the hexahydrated double selenates were read to the Royal Society on March 14th last, and published shortly afterwards.<sup>38</sup> They relate to the manganese and cadmium groups of double selenates. Sufficient was said in last year's report (pages 231 to 234) concerning this prolonged investigation—which includes not only this large group

S  
of monoclinic double salts,  $\text{R}_2\text{M}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ , but also the simple  
rhombic normal sulphates and selenates of the alkalis,  $\text{R}_2\overset{\text{S}}{\text{Se}}\text{O}_4$ .

<sup>35</sup> R. M. Bozorth, *J. Amer. Chem. Soc.*, 1922, **44**, 1066; *A.*, ii, 499.

<sup>36</sup> R. W. G. Wyckoff, *ibid.*, 1924; *A.*, ii, 765.

<sup>37</sup> A. F. Joffe and M. V. Kirpicheva, *Phil. Mag.*, 1922, [vi], **43**, 204.

<sup>38</sup> A. E. H. Tutton, *Proc. Roy. Soc.* 1922, [A], **101**, 225, 245; *A.*, ii, 502, 505.

75 salts in all having been very fully dealt with—to render more than passing notice in this Report superfluous. It will suffice to say that at the conclusion of the second (last) memoir, that on the cadmium group, six pages are devoted to a general review of the whole research, and are followed by a complete list (with references) of the separate memoirs, 26 in number, in which the results have from time to time been communicated, and of six others describing the new instruments devised for the work. The two main results which stand out are (1) the progression of the whole of the crystallographic and physical constants with the atomic number of the alkali metal, potassium, rubidium, or caesium, and (2) the iso-structure of the analogous rubidium and ammonium salts. But even the many minor results are proving of more than passing interest in the light of other contemporary research, especially that concerning the structure of the atom and that brought about by the advent of X-ray crystal analysis; and it is highly satisfactory that there is full agreement between all this that is fully substantiated and the writer's results. A quotation of the last paragraph of the final paper will perhaps best express it.

“Thus it has come about, by the time that the author has completed his crystallographic investigation of these important isomorphous series, that a full explanation of the results is afforded by the immense amount of real knowledge that has been accumulated during the same time concerning the structure and nature of the chemical atom, and that revealed by means of X-rays, from which the law of atomic diameters has been derived. It is thus highly satisfactory that the work of Moseley, Sir J. J. Thomson, Langmuir, the Braggs and the author should so perfectly agree in giving us a wider and fuller understanding of the nature of crystals, and of the structure of the solid matter of which they are the organised expression, than could have been expected or anticipated at the time when the author's researches on these isomorphous series were initiated.”

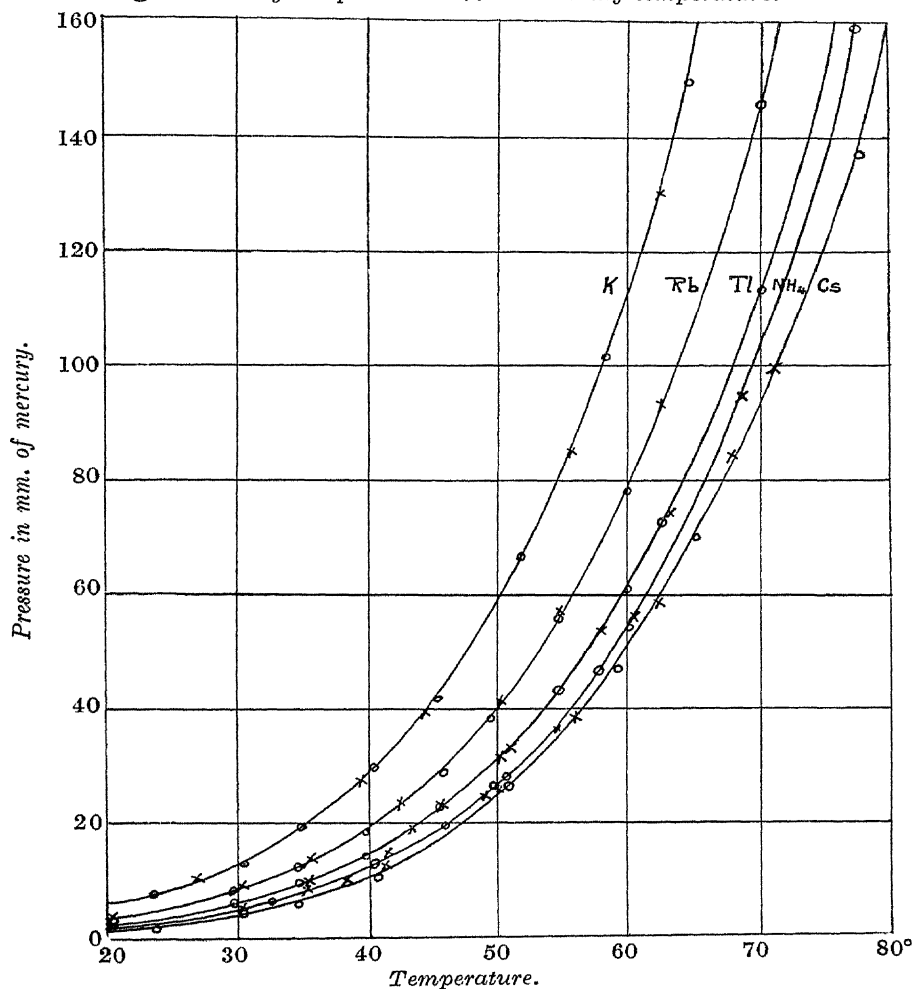
*The Dissociation Pressures of Hydrated Cupric Alkali Sulphates* is the subject of an interesting paper by R. M. Caven and J. Ferguson.<sup>39</sup> The salts investigated were the copper group of double sulphates,  $R_2SO_4 \cdot CuSO_4 \cdot 6H_2O$ , in which R is potassium, rubidium, caesium, ammonium, or thallium. The results agree with the writer's conclusion in the research just referred to, that there is a clear increase in the electropositive character of the alkali metal in passing from potassium, through rubidium, to caesium. They are expressed in the curves reproduced in Fig. 11. They indicate that the water of crystallisation is held more firmly, the greater the electropositive-

<sup>39</sup> R. M. Caven and J. Ferguson, *T.*, 1922, **121**, 1406.

ness of the alkali metal, and also that the heat evolved in the combination of the lower hydrate (with  $2\text{H}_2\text{O}$ ) with water also increases as the electropositive character of the alkali metal advances in

FIG. 11.

○ *Ascending temperature.* × *Descending temperature.*



Vapour Pressures of Copper Group of Double Sulphates.

strength. Moreover, the affinity of the process shows very markedly the same variation. The positions of thallium and ammonium relative to rubidium and caesium in the series of alkali metals, as determined by these experiments, accord with those assigned to them by the writer from observations of the morphological and

physical properties of their salts. This practically verbatim quotation from the conclusions of Caven and Ferguson forms a welcome confirmation from a new standpoint.

*A Crystallographic and Optical Study of some Inorganic Complex Salts* has been made by Miss Isabel E. Knaggs.<sup>40</sup> The first of the substances dealt with is potassium ferri-oxalate,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 3\text{H}_2\text{O}$ , which crystallises with holohedral monoclinic symmetry and has been already investigated by F. M. Jaeger, with whose data this new measurement agrees. The second substance is the analogous aluminium compound, in which aluminium replaces the iron, and which is shown to be truly isomorphous. A number of still more complicated compounds having *cis*- and *trans*- forms were investigated, and some rather surprising cases of apparent isomorphism observed.

At the meeting of the Mineralogical Society on November 7th, 1922, Miss Knaggs also gave an account of the crystals of some interesting carbon compounds of the four types  $\text{CX}_4$ ,  $\text{CX}_3\text{Y}$ ,  $\text{C}(\text{CX}_3)_4$ , and  $\text{C}(\text{CX}_2\text{Y})_4$ , where X and Y are other elements. Those of the first and third types, containing only one other element than carbon, appear to be usually cubic, while those of type 2 are trigonal or hexagonal, and those of type 4 tetragonal. The symmetry of the crystal thus resembles to a considerable extent that of the molecule, suggesting that there may be only one molecule in the crystal unit in these cases of more symmetrical molecules. It will be highly interesting to have these cases investigated by means of X-rays, so as to ascertain whether this is really the case, especially in the light of Shearer's rules.

#### *Physical-crystallographic Investigations.*

*The Piezo-electricity of Rochelle Salt* forms the subject of a paper by E. K. Scott.<sup>41</sup> Some large crystals, weighing 100 grams or more, were used, and the piezo-electric effect was very pronounced when they had received prolonged drying, first with alcohol and subsequently at 40°. Crystals showing "hour-glass" marking afforded the effect best of all, by the application of a twisting couple about the principal axis of the crystals. Potentials as high as 500 volts were developed. The crystals may be used for the reproduction and transmission of sounds.

*A New Optical Property of Biaxial Crystals* has been observed by C. V. Raman and V. S. Tamma,<sup>42</sup> using a plate of aragonite cut perpendicular to the acute bisectrix of the optic axial angle.

<sup>40</sup> (Miss) Isabel E. Knaggs, *T.*, 1922, 121, 2069.

<sup>41</sup> E. K. Scott, *Trans. Faraday Soc.*, 1922, 17, 748; *A.*, ii, 609.

<sup>42</sup> C. V. Raman and V. S. Tamma, *Phil. Mag.*, 1922, [vi], 43, 510.

Although the object used is a plate bounded by parallel faces, it forms a real erect image, with unit magnification, of a pinhole or other small source or object, illuminated with monochromatic light. If white light be used, a spectrum is afforded.

A luminous filament may be used instead of a pinhole, to vary the phenomena. The image is formed by light which travels through the crystal along an axis of single ray velocity.

*The Sizes of Atoms in Crystals.*—The values given by W. L. Bragg for the diameters of the atoms of such elements as have yet entered into crystals examined by X-rays, from which he deduced his important law of atomic diameters, and which were quoted on page 229 of the last Report, have on the whole been remarkably confirmed by work published during 1922. Thus R. N. Pease<sup>43</sup> finds the following interatomic distances, the values of Bragg being given afterwards in brackets: in diamond 1·54 (1·54), in silicon 2·30 (2·35), in grey tin 2·80 (2·80), in silicon carbide 1·92 (1·90), in zinc blende 2·41 (2·35), and in cuprous chloride 2·41 (2·43). Also an investigation of the viscosity of silicon hydride,  $\text{SiH}_4$ , by A. O. Rankine and C. J. Smith<sup>44</sup> has yielded further confirmation and support.

### *New Minerals.*

Quite a considerable number of new minerals have been announced during the year 1922, of which the following may be mentioned, including a rich find of radioactive minerals at Katanga in the Belgian Congo.

*Becquerelite*, described by A. Schoep,<sup>45</sup> is a radioactive mineral occurring at Katanga as yellow crusts of small orthorhombic crystals on pitchblende. It contains 86·5 per cent. of  $\text{UO}_3$ , and is practically  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ .

*Dewindtite*, also described by Schoep,<sup>46</sup> was also found at Katanga, and is a radioactive yellow powder of the composition  

$$4\text{PbO} \cdot 8\text{UO}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 12\text{H}_2\text{O}.$$

*Soddite*, also a radioactive mineral from Katanga described by the same author,<sup>47</sup> occurs as orthorhombic crystal aggregates of the composition  $12\text{UO}_3 \cdot 5\text{SiO}_2 \cdot 14\text{H}_2\text{O}$ .

*Stasite*, found at Kasola, Katanga, again described by Schoep,<sup>48</sup> has the same composition as dewindtite, the substance being di-

<sup>43</sup> R. N. Pease, *J. Amer. Chem. Soc.*, 1922, **44**, 769; *A.*, ii, 428.

<sup>44</sup> A. O. Rankine and C. J. Smith, *Proc. Physical Soc.*, 1922, **34**, 181; *A.*, ii, 709.

<sup>45</sup> A. Schoep, *Compt. rend.*, 1922, **174**, 1240; *A.*, ii, 450.

<sup>46</sup> *Idem*, *ibid.*, 623; *A.*, ii, 305.

<sup>47</sup> *Idem*, *ibid.*, 1066; *A.*, ii, 451.

<sup>48</sup> *Idem*, *ibid.*, 875; *A.*, ii, 386.



morphous. It occurs as golden-yellow, flat prisms, and also differs in density from dewindtite, as well as in crystal form and in colour.

*Ceruleofibrite*, described by E. F. Holden,<sup>49</sup> is a basic chloroarsenate of copper,  $\text{CuCl}_2 \cdot \frac{1}{3} \text{Cu}_3 \text{As}_2 \text{O}_8 \cdot 6 \text{Cu}(\text{OH})_2$ , which was found as radiating tufts of bright blue fibres, orthorhombic needles, on cuprite from Arizona.

*Gillespite*, described by W. T. Schaller,<sup>50</sup> was found in an Alaskan moraine as scaly masses, and appears to have the composition  $\text{Fe}''\text{BaSi}_4\text{O}_{10}$ .

*Sincosite*, also described by Schaller,<sup>51</sup> is a hydrous calcium vanadyl phosphate,  $\text{CaO} \cdot \text{V}_2\text{O}_4 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , from Sincos, Peru. It forms uniaxial plates belonging to the uranite group.

*Melanovanadite*, described by W. Lindgren, L. F. Hamilton, and C. Palache,<sup>52</sup> occurs as bunches of black, monoclinic needles on a black shale from Minasragra, Cerro de Pasco, and has the composition  $2\text{CaO} \cdot 3\text{V}_2\text{O}_5 \cdot 2\text{V}_2\text{O}_4$ .

*Thorveitite* is a silicate of scandium found at Sætersdalen, Norway, in large, greyish-green, monoclinic prismatic crystals resembling epidote. It appears to be  $(\text{Sc}, \text{Y})_2\text{Si}_2\text{O}_7$ , analogous to thalenite. It was discovered and described by J. Schetelig.<sup>53</sup>

#### *New Books and Editions.*

Prof. F. Rinne (Leipzig) has produced during 1922 new editions of his two books "Das feinbauliche Wesen der Materie nach dem Vorbilde der Kristalle," published by Gebrüder Borntraeger, Berlin, and "Kristallographische Formenlehre und Anleitung zu kristallographisch-optischen röntgenographischen Untersuchungen," published by Max Janecke, Leipzig. The former contains excellent portraits of von Groth, Haüy, Schoenflies, Fedorov, Tschermak, von Laue, Debye, Scherrer, Sir W. H. Bragg, and W. L. Bragg. It is full of illustrations and diagrams of an original character, including many of Prof. Rinne's own X-radiograms of crystals. It regards the whole achievement of X-ray analysis as having revealed the true nature of the fine structure of solid matter. The second and later book is also very original inasmuch as it gives a readable account of crystal phenomena and ordinary elementary Crystallography from the aspect of one steeped in the later X-ray analytical work.

In July there was published by Thomas Murby & Co. a book of 152 pages by Mr. T. V. Barker, Lecturer in Chemical Crystallo-

<sup>49</sup> E. F. Holden, *Amer. Min.*, 1922, 7, 80; *A.*, ii, 516.

<sup>50</sup> W. T. Schaller, *J. Washington Acad. Sci.*, 1922, 12, 7.

<sup>51</sup> *Idem*, *ibid.*, 12, 195; *A.*, ii, 450.

<sup>52</sup> W. Lindgren, L. F. Hamilton, and C. Palache, *Amer. J. Sci.*, 1922, [v], 3, 195; *A.*, ii, 305.

<sup>53</sup> J. Schetelig, *Norsh. Geol. Tidsskr.*, 1922, 6, 233; *A.*, ii, 306.

graphy at Oxford, on "Graphical and Tabular Methods in Crystallography." In it are described the methods of crystallographic practice which Mr. Barker has made his own, largely following the methods of V. Goldschmidt and Fedorov, especially those involving rapidity of work and concise expression. It is a most valuable compendium of the more recent and useful graphical methods.

A so-called "third" edition by W. E. Ford of Dana's "Text Book of Mineralogy," with an extended treatise on crystallography and physical mineralogy, has been published in New York. It forms a rejuvenated, very much enlarged, and fairly up-to-date revision of the great text book of 1877, the total issues of which in its many editions and re-issues are estimated to have reached 27,000.

The second edition of the writer's "Crystallography and Practical Crystal Measurement" was published by Messrs. Macmillan and Co. in March, in two volumes of 760 and 686 pages respectively, the first edition having been comprised in one volume of 946 pages. Each volume is in two parts, the total of 60 chapters being thus divided into four parts. These are: Part I, Crystal Form and Goniometry; Part II, Crystal Structure and its X-Ray Analysis; Part III, Crystal Optics and Microscopy; and Part IV, Crystal Chemistry, Deformational Physics and its Interferometry.

A ninth List of new Mineral Names, by Dr. L. J. Spencer, was issued in 20 pages with the September number of the *Mineralogical Magazine*. A concise description is given of each of the minerals included. Mineralogists and crystallographers are again indebted to Dr. Spencer not only for this further most useful, long list, but, with some assistance from collaborators, for the *Mineralogical Abstracts*, which are now regularly issued by the Mineralogical Society, with the *Mineralogical Magazine*. Volume I of these Abstracts, just completed, contains no fewer than 1254 abstracts, extending from the year 1915 to 1922. In spite of the considerable cost entailed by their publication, it is very satisfactory that the Society has decided to continue this most valuable addition to the magazine.

#### *Concluding Remarks.*

In concluding this epitome of the crystallographic and mineralogical work of the year 1922, mention should be made of the highly interesting special number of "Die Naturwissenschaften" entitled "Zehn Jahre Laue-Diagramm," which was issued in April, containing eight articles by authors who have contributed to the subject of the X-ray analysis of crystals since its inception by Dr. M. von Laue in the year 1912. They include Prof. von Laue's collaborators

in the first discovery, Drs. Friedrich and Knipping. The former gives a most interesting account of the circumstances of the original discovery, in the midst of the remarkable coterie of experts at that time in Munich, which included Röntgen, von Groth, Ewald, Sommerfeld, and Laue. The origin appears to have been a discussion between Laue and Ewald as to how the minuter electromagnetic waves would behave with gratings of a similar small order of dimensions, and an enthralling description is given of the excitement among the whole scientific circle at Munich when the experiment was tried by Friedrich and, after a preliminary failure owing to not having hit off the right conditions, so admirably succeeded, and the diffraction or reflection of X-rays by the planes of atoms in crystals became an accomplished fact. Indeed, the excitement was still high when, that same summer, both Fedorov and the writer visited von Groth at Munich, and were shown the first X-radiograms of zinc blende.

This Report is but a very inadequate attempt to do justice to the amount of valuable research which has been carried out during the year 1922. But sufficient will doubtless have been written to show that the tenth anniversary of the inauguration of this new weapon of research, and the centenary of Pasteur, the discoverer of the true nature of tartaric acid and of the meaning of its optical activity, is marked by a richness of result that the discoverers in the years 1912 and 1848 respectively could never have foreseen, still less have anticipated; and that the promise of a still richer harvest yet to be gleaned by the earnest workers of the future is so bright and alluring as to afford the highest encouragement to those who are making this branch of natural knowledge their special domain.

A. E. H. TUTTON.

## SUB-ATOMIC PHENOMENA AND RADIOACTIVITY.\*

### *Introduction.*

UNDER the title "Sub-atomic Phenomena and Radioactivity" are included in a broad sense all phenomena directly associated with the central nuclei of atoms, as opposed to the so-called chemical phenomena which we now know to be connected with the behaviour of the planetary electrons occupying the outer domains of these atoms. This Report will therefore be concerned with the masses of individual atoms determined by physical means, the isotopic constitution of the chemical elements, and their spectra, in so far as these are affected by isotopy. It will also deal with work on the constitution of the nuclei themselves and the manner in which they may be disintegrated artificially. All phenomena connected with the spontaneous disintegration of the more complicated nuclei are, of course, included in radioactivity.

During the past two years advances have been made in all these branches and some valuable steps taken towards elucidating the structure of the nucleus itself. Among the more important of these should be mentioned the studies on artificial disintegration and other phenomena of nuclear collision made by Rutherford and his colleagues, and the application of the quantum theory to explain the relation between  $\beta$ -rays and the  $\gamma$ -rays which produce them, by Ellis and others. Progress in this direction is also promised by the discovery of divergences from the whole-number rule, but the accuracy of comparison of atomic masses will have to be advanced considerably beyond that at present available before much information will be obtainable from this line of attack.

### *The Isotopic Constitution of the Elements.*

The work in this field during 1921 has been already summarised in the Report for that year.<sup>1</sup> During 1922, several more elements have been successfully investigated and other additional results obtained. Dempster has applied his method of positive ray analysis to calcium and zinc, and the composition of five more elements has been determined by means of the mass-spectrograph. The theory of the latter instrument has been satisfactorily worked

\* This Report covers the years 1921 and 1922.

<sup>1</sup> *Ann. Rep.*, 1921, 18, 34—35.

out mathematically<sup>2</sup> and a notable advance in its technique has been made by the use of specially treated photographic plates. These results are summarised below.

*Aluminium.*—Results obtained by the mass-spectrograph when pure chlorine was present in the discharge tube and had reacted with the aluminium electrodes leave very little doubt as to the constitution of this metal. Aluminium may be regarded as a simple element of atomic weight 27, as its chemical atomic weight would lead us to suspect.<sup>3</sup>

*Calcium.*—By the treatment of this metal in the same way as magnesium<sup>4</sup> Dempster<sup>5</sup> has been able to show that calcium has a principal isotope 40 with a weaker component 44.

*Chlorine.*—It is now reasonably certain that this element does not contain any appreciable quantity of an isotope 39.<sup>6</sup>

*Iron.*<sup>7</sup>—This element has been investigated by means of its volatile pentacarbonyl. Its mass-spectrum is characterised by a strong line at 56 and possibly a very faint one at 54. The measurements on the former indicate a value slightly less than a whole number, but the divergence is within the experimental error.

*Zinc.*—This metal was analysed by Dempster at the same time as calcium. The results indicate that it consists of four isotopes the masses of which, by comparison with the calcium line 40, are given as 64, 66, 68, and 70. The first appears the strongest component and the last is very feeble.

*Selenium.*<sup>8</sup>—The mass-spectra of selenium were obtained by a special device by which the element itself was vaporised in the discharge tube. The results were very definite and show that it consists of six isotopes 74, 76, 77, 78, 80, 82. Isotope 74 is only present in minute proportion. No divergence from the whole-number rule could be detected.

*Tin.*<sup>9</sup>—By the use of its volatile methide, this element has been shown to consist of seven, or possibly eight, isotopes, as given in the following table. Measurement of their masses indicates that, although their differences are integral to the highest accuracy, the masses themselves tend to be 2 to 3 parts in 1000 less than whole numbers on the oxygen scale. This is the first definite divergence observed since that of hydrogen, and it cannot be attributed to experimental error in measurement on the following account. The

<sup>2</sup> F. W. Aston and R. H. Fowler, *Phil. Mag.*, 1922, [vi], 43, 514; *A.*, ii, 241.

<sup>3</sup> F. W. Aston, *Nature*, 1922, 110, 664; *A.*, ii, 844.

<sup>4</sup> *A.*, 1921, ii, 402.

<sup>5</sup> *Physical Rev.*, 1922, 20, 631.

<sup>6</sup> F. W. Aston, *Nature*, 1922, 110, 664; *A.*, ii, 844.

<sup>7</sup> *Idem*, *ibid.*, 312; *A.*, ii, 710.

<sup>8</sup> *Idem*, *ibid.*, 664; *A.*, ii, 844.

<sup>9</sup> *Idem*, *ibid.*, 109, 813; *A.*, ii, 650.

lines of xenon were present on the plate, hence the line 135 due to  $\text{Sn}^{120}\text{CH}_3$  should have appeared exactly half-way between the two strong xenon lines 134 and 136. It was actually unmistakably nearer the former. Whether this large divergence, which is about 0.3 in atomic weight, represents the accumulated divergence of both elements, cannot be settled, although it is most probable that tin diverges more from a whole number than xenon. In any case, it is remarkable that it should occur in two elements so near in atomic number as tin and xenon.

*Antimony.*<sup>10</sup>—The mass-spectrum of antimony consists of two strong lines, 121, 123, the former being slightly the more intense. Very faint lines also appear at 122, 124, but these are ascribed to hydrides. The masses of the two isotopes of antimony are probably slightly less than whole numbers. The results show that the old value for the atomic weight, 120.2, is definitely wrong, but they are in good agreement with the value recently obtained by Willard and McAlpine.

*Xenon.*—The mean atomic weight of this element estimated from its mass-spectrum is distinctly higher than the accepted value obtained from the density by Moore.<sup>11</sup> In order to ascertain whether the discrepancy could be put down to the presence of krypton as an impurity, a sample of the actual gas used in the density determinations was analysed by means of the mass-spectrograph. The results showed no appreciable presence of krypton, so that the difference remains unexplained. The two doubtful isotopes, 128, 130, have been confirmed,<sup>12</sup> and two extremely faint probable additional ones have been detected at 124, 126.<sup>13</sup>

From the table of results on p. 270, some interesting statistical relations are at once apparent. In the nucleus of the atom there is never less than one electron to every two protons; in other words, the atomic weight of the lightest isotope of an element cannot be less than twice its atomic number, except in the case of hydrogen. The excess of the atomic weight over twice the atomic number has been called the isotopic number by Harkins. The number of isotopes of any one element shows definite limits and tends to increase with atomic number. It is also greater for elements of even than for those of odd atomic number; in the latter case, it is never greater than two. The number of electrons in the nucleus tends to be even, that is, in the majority of cases even atomic number is associated with even atomic weight and odd

<sup>10</sup> F. W. Aston, *Nature*, 1922, **110**, 732; *A.*, 1923, ii, 32.

<sup>11</sup> "Isotopes," p. 114.

<sup>12</sup> F. W. Aston, *Nature*, 1922, **109**, 813; *A.*, ii, 650.

<sup>13</sup> *Idem*, *ibid.*, **110**, 664; *A.*, ii, 844.

*Table of Elements and Isotopes.*

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Masses of isotopes in order of intensity.
H	1	1.008	1	1.008
He	2	3.99	1	4
Li	3	6.94	2	7, 6
Gl	4	9.1	1	9
B	5	10.9	2	11, 10
C	6	12.00	1	12
N	7	14.01	1	14
O	8	16.00	1	16
F	9	19.00	1	19
Ne	10	20.20	2	20, 22
Na	11	23.00	1	23
Mg	12	24.32	3	24, 25, 26
Al	13	26.96	1	27
Si	14	28.3	2	28, 29, (30)
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37
A	18	39.88	2	40, 36
K	19	39.10	2	39, 41
Ca	20	40.07	(2)	40, 44
Fe	26	55.84	(1)	56, (54) ?
Ni	28	58.68	2	58, 60
Zn	30	65.37	(4)	64, 66, 68, 70
As	33	74.96	1	75
Se	34	79.2	6	80, 78, 76, 82, 77, 74
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80, 78
Rb	37	85.45	2	85, 87
Sn	50	118.7	7 (8)	120, 118, 116, 124, 119, 117, 122, (121)
Sb	51	121.77	2	121, 123
I	53	126.92	1	127
X	54	130.2	7 (9)	129, 132, 131, 134, 136, 128, 130, (126), (124)
Cs	55	132.81	1	133
Hg	80	200.6	(6)	(197—200), 202, 204

(Numbers in brackets are provisional only.)

with odd. If we plot the first 40 natural numbers and show those occupied by known elements as in the figure, a curious relation

H			He		Li	Li		Gl	B	B	C		N		O		F	Ne		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
1	Ne	Na	Mg	Mg	Mg	Al?	Si	Si	Si?	P	S				Cl	A	Cl		K	A
21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	

may be noticed, namely, that the simple recurring series 2, 3, 5, 8 —, of which each term is the sum of the two previous terms, is in every case, up to 34, represented by a gap. This relation may break down at the next term, if manganese has an isotope 55, but this is not yet known.

*Isobares.*—These are substances having the same atomic weight

but different chemical properties. They have been well known for some years among the radioactive elements, but among the non-radioactive ones, although it was perfectly certain they must exist, none was actually observed until Dempster showed that the principal isotope of calcium had an atomic weight 40 and so was isobaric with the principal isotope of argon. Since then, the seleniums 78, 80, 82 have been found isobaric with kryptons, and one tin 124 with a probable xenon. If we disregard the doubtful isobaric pair Sb, Sn 121, every pair has for one of its members an inert gas, and all the isobares (including the radioactive ones) have atomic weights which are even numbers.

*Periodic Systems of Elements and Isotopes.*

Many new periodic systems of the elements have been put forward by Bourgerel,<sup>14</sup> Oddo,<sup>15</sup> Partington,<sup>16</sup> Kirchhof,<sup>17</sup> Masson,<sup>18</sup> Broek,<sup>19</sup> Kohlweiler,<sup>20</sup> and others. Some of these are worked out theoretically on some physical basis, for example, the purely speculative idea that all elements are the results of radioactive disintegrations. Others are convenient schemes of representing the numerical values obtained by experiment in such a way as to bring out certain interesting points. The most complete scheme of this kind is that of Harkins, which has been elaborated by him in numerous publications<sup>21</sup> to which the reader is referred. In a valuable table given in one of his most recent papers<sup>22</sup> is to be found a remarkably complete summary of the facts and reasonable speculations in this field. In this diagram, against their atomic numbers, are plotted the "isotopic numbers" of all atomic species known and probable. They lie in a band of roughly parabolic curvature which widens as it gets further from the origin. The probable constitutions of elements, not experimentally analysed at the time the scheme was drawn up, are admittedly speculative and dependent on the trustworthiness of the chemical atomic weight determinations. The accuracy of the predictions in the cases of selenium and antimony is very striking at first sight, and shows how much can be done by the judicious use of general and statistical relations such as those given in the previous paragraph.

<sup>14</sup> *Mon. Sci.*, 1920, **10**, 241; *A.*, 1921, ii, 102.

<sup>15</sup> *Gazzetta*, 1920, **50**, 213; *A.*, 1921, ii, 102.

<sup>16</sup> *Chem. News*, 1920, **121**, 304; *A.*, 1921, ii, 103.

<sup>17</sup> *Physikal. Z.*, 1920, **21**, 711; *A.*, 1921, ii, 103.

<sup>18</sup> *Phil. Mag.*, 1921, [vi], **41**, 281; *A.*, 1921, ii, 191.

<sup>19</sup> *Physikal. Z.*, 1921, **22**, 164; *A.*, 1921, ii, 295.

<sup>20</sup> *Ibid.*, 243; *A.*, 1921, ii, 689.

<sup>21</sup> *A.*, 1921, ii, 445, 583, 690; 1922, ii, 490, 702.

<sup>22</sup> W. D. Harkins, *J. Franklin Inst.*, 1922, **194**, 645.



*The Constancy of Chemical Atomic Weight and the Relation of the Latter to the Mean Weight deduced from the Results of the Mass-spectrograph.*

As soon as the isotopic nature of some common and widely distributed elements had been definitely proved, it became of interest to determine with the greatest care the atomic weights of such complex elements from sources as widely distributed as possible. Differences might be expected from two causes; either the process of origin of the element might be different at different points of the earth's surface, yielding isotopes in different proportions, or elements of the same original constitution might have their mean weight changed by some natural process which tended to bring about partial separation of the constituent isotopes. Several pieces of work have been performed with a view to test this point. Baxter and Parsons<sup>23</sup> compared the atomic weight of nickel from meteorites with that of ordinary terrestrial nickel, but no difference was found beyond that expected from experimental error. (Mlle) Curie has compared the atomic weight of chlorine from several minerals with that of chlorine from sea-water. In the case of two, the marine origin of which was in the highest degree unlikely, no difference was found. Chlorine prepared from a sample of sodium chloride obtained from a desert region in Central Africa gave a value slightly above normal.<sup>24</sup> Chlorine from an ancient mineral, apatite, from Balme has also been investigated<sup>25</sup>; no difference from normal chlorine could be detected. Taking into consideration the age and origin of the mineral, it may be concluded that the chlorine at the time of the formation of the minerals of the primary magma contained the two isotopes in the same proportion as it does to-day, or that the two isotopes were then formed in constant proportions.

Boron is an element well suited for this test, for its isotopes differ by 10 per cent. in mass and are both present in considerable proportion. Monro<sup>26</sup> has compared the atomic weight of boron from some New Zealand minerals with that of the element obtained from pure sodium borate; here again no difference could be detected. Finally, Brönsted and Hevesy<sup>27</sup> measured the density of mercury from minerals of different origin and found no divergence higher than that corresponding with a difference in atomic weight of 0.0004—0.0012.

<sup>23</sup> *J. Amer. Chem. Soc.*, 1921, **43**, 507; *A.*, 1921, ii, 338.

<sup>24</sup> Mlle Irene Curie, *Compt. rend.*, 1921, **172**, 1025; *A.*, 1921, ii, 396.

<sup>25</sup> Mlle Ellen Gleditsch and B. Samdahl, *ibid.*, 1922, **174**, 746; *A.*, ii, 281.

<sup>26</sup> *T.*, 1922, **121**, 986.

<sup>27</sup> *Nature*, 1922, **109**, 813; *A.*, ii, 645.

The accumulation of negative evidence of this kind is very impressive, and supports the idea, already put forward, that the evolution of the elements (apart from those produced by radioactive disintegration) must have been such as to lead to a proportionality of isotopes of the same element which was constant from the start, and since we know of no natural process of separation, has remained constant ever since.

Although no accurate determinations of the relative intensity of mass-spectrum lines has yet been carried out, their relative strengths can be approximately estimated. Hence the mean atomic weight of a complex element can be deduced in some cases with considerable accuracy, and therefore provides a valuable check on the figure obtained by the ordinary chemical methods. In most cases, the agreement has been good, but in a few the discrepancy is considerable.<sup>28</sup> It is satisfactory to note that during the past year redeterminations<sup>29</sup> of the chemical atomic weights have removed the discrepancy in several cases. Thus the revision of the atomic weight of boron by two independent determinations<sup>29</sup> gives 10.83 and 10.82, respectively, figures agreeing much better with that estimated from the mass-spectrum,  $10.75 \pm 0.07$ , than did the previous values, 11.0 and 10.90. Again, positive ray results<sup>30</sup> indicate that glucinum is a simple element, whereas the old value for the atomic weight, 9.1, differs so far from a whole number as virtually to deny this possibility. This discrepancy has now been removed by the redetermination of the chemical atomic weight by Hönigschmid and Birckenbach,<sup>31</sup> who obtain a value 9.018. The cases of antimony and xenon have already been alluded to, that of krypton is still unexplained.

*Atomic Volume of Isotopes.*—Soddy<sup>32</sup> has compared the values obtained for the density and atomic weight of ordinary lead; lead from thorite, and lead from uranium minerals. He concludes that the atomic volumes cannot differ by so much as three parts in ten thousand and the atomic diameters by so much as one part in ten thousand.

### *The Spectra of Isotopes.*

*Series Spectra.*—Merton has repeated his experiments on the isotopes shift of the line  $\lambda$  4058 of lead<sup>33</sup> and extended his measure-

<sup>28</sup> See F. W. Aston, "Isotopes" (Arnold, 1922), p. 114.

<sup>29</sup> G. P. Baxter and A. F. Scott, *Science*, 1921, **54**, 524; *A.*, ii, 285; O. Hönigschmid and L. Birckenbach, *Anal. Fis. Quim.*, 1922, **20**, 167; *A.*, ii, 641.

<sup>30</sup> G. P. Thomson, *Phil. Mag.*, 1921, [vi], **42**, 857; *A.*, 1921, ii, 675.

<sup>31</sup> *Ber.*, 1922, **55**, [B], 4; *A.*, ii, 214.

<sup>32</sup> *Nature*, 1921, **107**, 41; *A.*, 1921, ii, 698.

<sup>33</sup> *Ann. Rep.*, 1920, **17**, 224.

ments to other lines. Using a very pure sample of uranium lead from Australian carnotite, he obtained the results indicated in the following table :<sup>34</sup>

$\lambda$	$\left[ \begin{array}{c} \lambda(\text{Carnotite lead}) \\ -\lambda(\text{ordinary lead}) \end{array} \right]$	$\left[ \begin{array}{c} \text{Wave number (ordinary lead)} \\ -\text{Wave-number (carnotite lead)} \end{array} \right]$
4058	$0.011 \pm 0.0008$	$0.065 \pm 0.005$
3740	$0.0074 \pm 0.0011$	$0.053 \pm 0.008$
3684	$0.0048 \pm 0.0007$	$0.035 \pm 0.005$
3640	$0.0070 \pm 0.0003$	$0.052 \pm 0.002$
3573	$0.0048 \pm 0.0005$	$0.037 \pm 0.004$

It will be noticed that the shift for the line  $\lambda$  4058 is rather more than twice that obtained before. Merton suggests that the most probable explanation of this difference is that the carnotite lead used was a purer sample of uranium lead than that obtained from the pitchblende residues. It is also apparent that the differences are not the same for different lines, an interesting and somewhat surprising result.

McLennan and Ainslie<sup>35</sup> have subjected the light from a strong lithium arc to the highest resolution and find that the line  $\lambda$  6708 consists of a close quartet with separations of 0.128 Å., 0.173 Å., and 0.165 Å. He suggests that these are the doublets of the isotopes of lithium,  $\text{Li}^6$  and  $\text{Li}^7$ , although the intensity relations between them are by no means in accordance with this view unless a new theory is adopted. He proposes that, from these displacements and the displacements in the case of lead, the isotope displacements can be very closely obtained by multiplying the displacement calculable on the Bohr theory by the atomic number of the respective elements. In a later paper<sup>36</sup> on the absorption of  $\lambda$  5460.97 by luminous mercury vapour, he describes satellites which he considers are due to the isotopes of mercury and quotes displacements agreeing with the empirical rule given above, but here again the intensity relations are not satisfactory. Merton,<sup>37</sup> recently commenting on these results, points out that the measurements of the enhanced lines of helium agree perfectly with the Bohr theory, and therefore definitely contradict McLennan's rule connecting atomic number with displacement. He also raises several exceedingly strong arguments against the possibility of the lithium doublets being in any way connected with the isotopic constitution of that element.

The difference between series spectra of isotopes is discussed gener-

<sup>34</sup> *Proc. Roy. Soc.*, 1921, [A], 100, 84; *A.*, 1921, ii, 611.

<sup>35</sup> *Ibid.*, 1922, [A], 101, 342; *A.*, ii, 541.

<sup>36</sup> J. C. McLennan, D. S. Ainslie, and (Miss) F. M. Cale, *Proc. Roy. Soc.*, 1922, [A], 102, 33; *A.*, ii, 728.

<sup>37</sup> *Nature*, 1922, 110, 632; *A.*, ii, 803.

ally by Ehrenfest,<sup>38</sup> Bohr,<sup>39</sup> and Nicholson.<sup>40</sup> Ehrenfest maintains that the ordinary Bohr formula,  $\nu_2 : \nu_1 = M_2/M_2 + m : M_1/M_1 + m$ , where  $M_1$ ,  $M_2$ , and  $m$  are respectively the masses of the nuclei of the isotopes, and of the electron, and  $\nu_1$  and  $\nu_2$  the frequencies of the corresponding lines, cannot be true in general. Bohr admits that the effect of the mass of the nucleus on the spectrum of an atom containing more than one electron is a complex problem; not only may the mass effect disappear completely, but also may be different from that calculated for an atom with one electron. Nicholson points out that the large separation observed by McLennan in lithium cannot be explained by the quantum theory, and suggests that the new series may be a combination series or a spark series.

*Band Spectra.*—The wave-lengths of the higher members of the band spectrum of uranium lead and ordinary lead have been compared by Grebe and Konen.<sup>41</sup> The chosen wave-lengths lie between 4257.690 and 4281.458 Å.U. Measurements of eighteen lines show that the wave-length of the line corresponding with uranium lead is on the average 0.055 Å.U. shorter than that for ordinary lead. This figure agrees so far as its order is concerned with the assumption that the diatomic molecules are the carriers of the band spectrum.

*Infra-red Spectra.*—The extreme smallness of the isotope shift expected in the spectra discussed above is due to the fact that one unit of the vibrating system is the electron itself, the mass of which is extremely small compared with that of the other unit, the nucleus. Very much larger effects are to be expected where two nuclei are concerned. Loomis<sup>42</sup> shows that the doubling of the absorption bands in the infra-red spectrum of hydrogen chloride, first observed by Imes, can be explained on this view and gives a very satisfactory confirmation of the isotopic nature of chlorine. The frequencies of the doublets due to isotopes should be approximately proportional to  $\sqrt{(m_1 + m_2)/m_1 m_2}$ , where  $m_1$  is the mass of the hydrogen nucleus and  $m_2$  the mass of the charged halogen atom; hence the band lines should differ by 1/1330. The average interval measured was 14 Å.U. or 4.5 wave numbers, which agrees with the calculated value of 4.3 wave numbers. Hydrogen fluoride does not show this effect, and in the case of hydrogen bromide the computed separations are too small to be observed as yet.

<sup>38</sup> *Nature*, 1922, **109**, 745; *A.*, ii, 598.

<sup>39</sup> *Ibid.*, 746; *A.*, ii, 598.

<sup>40</sup> *Ibid.*, 1922, **110**, 37; *A.*, ii, 599.

<sup>41</sup> *Physikal. Z.*, 1921, **22**, 546; *A.*, ii 4.

<sup>42</sup> *Astrophys. J.*, 1920, **52**, 248.

*Separation of Isotopes.*

Much work on the artificial separation of isotopes has been performed during the past two years, but nevertheless success has only been achieved in the case of two elements, mercury and chlorine. The work of Brönsted and Hevesy on the former<sup>43</sup> is particularly convincing both on account of the beauty and simplicity of the method used and the remarkable fidelity with which the results follow the theory, also fortunately simple. They found that if mercury is distilled at so low a pressure that molecules escaping from the surface of the liquid never return, and if at the same time the rate of distillation is kept down to a point at which the mixing of the liquid by self-diffusion is practically perfect, then the molecules of the different isotopes distil at rates inversely proportional to the square roots of their masses. In consequence, the lighter isotopes tend to increase in the first fractions and the heavier ones in the last residues of the distillation process. In their final work, 2700 c.c. of mercury were fractionated systematically to about 1/100,000 of the original volume in each direction. The density of the original mercury being taken as unity, the lighter fraction (0.2 c.c.) had a density 0.99974, and the heavier (0.3 c.c.) 1.00023. This corresponds with a difference of 0.1 of a unit in atomic weight. Using the same method with a solution of hydrochloric acid, they were later able to obtain evidence of a separation corresponding with 0.024 of a unit in the atomic weight of chlorine.<sup>44</sup> Egerton<sup>45</sup> announces a partial separation of the isotopes of zinc by the same method.

A change of about 0.05 of a unit has been achieved by Harkins<sup>46</sup> and Anson Hayes,<sup>47</sup> who used a method of diffusion through pipe-clay similar to that originally used in the separation of the isotopes of neon.<sup>48</sup> The system of diffusion was elaborate, large quantities of material were employed, and the experiments occupied a long period. In this and in a later communication,<sup>49</sup> the theory of the resolution of isotopic mixtures by diffusion is discussed at some length and it is suggested that slight separation of isotopes occurs during ordinary distillation under reduced pressure. Mulliken<sup>50</sup> gives a very complete theory of the separation of isotopes by thermal

<sup>43</sup> *Z. physikal. Chem.*, 1921, **99**, 189; *Phil. Mag.*, 1922, [vi], **43**, 31; *A.*, ii, 140.

<sup>44</sup> *Nature*, 1921, **107**, 619; *A.*, ii, 280.

<sup>45</sup> *Ibid.*, 1922, **110**, 773; *A.*, 1923, ii, 28.

<sup>46</sup> *J. Amer. Chem. Soc.*, 1921, **43**, 1803; *A.*, ii, 140.

<sup>47</sup> *Ibid.*

<sup>48</sup> *A.*, 1919, ii, 209.

<sup>49</sup> R. S. Mulliken and W. D. Harkins, *ibid.*, 1922, **44**, 37; *A.*, ii, 295.

<sup>50</sup> *Ibid.*, 1933; *A.*, ii, 492.

diffusion and by centrifuging, and shows that the latter method is likely to be of more value in the case of isotopes of high atomic weight. A special method, named evaporative centrifuging, is proposed whereby gas condensed in the periphery of the centrifuge at high speed would be allowed to evaporate very slowly, the light fractions being drawn off very gradually at low pressure from the centre of the apparatus. It is suggested that this method ought to yield a separation ten to fifteen times as great in one operation as would diffusion or evaporation. He also discusses the possibility of separating liquid isotopes by centrifuging, a method which has been considered by Poole.<sup>51</sup> An attempt to test this theory in the case of mercury proved unsuccessful, and its failure is attributed to slight vibration of the centrifuge.

Kohlweiler<sup>52</sup> still maintains the opinion that he has separated the isotopes of iodine, although the existence of these is contrary to the direct evidence of the mass-spectrograph. He ascribes his results to isotopes present in too small quantities to be detected by that apparatus. If this is the case, it is very difficult to understand how it could be possible to obtain the relatively enormous shift—0.88 of a unit—claimed, by any diffusion method.

Perhaps the most surprising report is that from Dublin claiming the separation of lead isotopes by chemical means.<sup>53</sup> Lead chloride was prepared from a mixture of ordinary lead and thorium lead, and the reaction represented by the equation  $2\text{PbCl}_2 + 4\text{MgRX} = \text{R}_4\text{Pb} + 2\text{MgCl}_2 + 2\text{MgX}_2 + \text{Pb}$  carried out. The lead tetraethyl and metallic lead constitute the fractions which are used separately in a repetition of the process. By two repetitions a separation indicated by relative atomic weights 207.1 and 207.4 is claimed. This result will need very strong confirmation before it is generally accepted, for the method is founded on an observation of Hoffmann and Wolf<sup>54</sup> in 1907 that a large separation of lead from radium-D could be effected by a single reaction with magnesium phenyl bromide. This statement was in direct contradiction to all the work of the most careful experimenters at that date, it has never been confirmed since, and is regarded by the most competent authorities in radioactivity to-day as probably erroneous.

Other possible methods of separation have been put forward. Skaupy<sup>55</sup> suggests that the differential effect of electronic impacts

<sup>51</sup> *Phil. Mag.*, 1921, [vi], **41**, 818; *A.*, 1921, ii, 403.

<sup>52</sup> *Z. physikal. Chem.*, 1922, **101**, 218; *A.*, ii, 497.

<sup>53</sup> T. Dillon, R. Clarke, and V. M. Hinchy, *Sci. Proc. Royal Dublin Soc.*, 1922, **17**, 53; *A.*, ii, 710.

<sup>54</sup> *Ber.*, 1907, **40**, 2425.

<sup>55</sup> *Z. Physik*, 1920, **2**, 213; *A.*, 1921, ii, 154.

in an electric discharge would give a separation of isotopes of the rare gases. Ludlam<sup>56</sup> describes experiments carried out to test a method of separation of the isotopes of chlorine based on a suggestion made by Sir J. J. Thomson that the number of impacts per second of the molecules of a gas on a surface will be in the inverse square root of their mass. Hydrogen chloride at a pressure of a few centimetres of mercury was passed over (a) a water surface, and (b) ammonia gas, and a small fraction allowed to remain uncombined. No change in molecular weight was observed after either process. An ingenious photochemical process has also been investigated.<sup>57</sup> If chlorine consists essentially of a mixture of three parts of  $\text{Cl}^{35}$  and one part of  $\text{Cl}^{37}$ , the molecules should be present in the proportions  $\text{Cl}^{35}_2 : \text{Cl}^{35}\text{Cl}^{37} : \text{Cl}^{37}_2 = 9 : 6 : 1$ . If light which has passed through a column of such chlorine enters a mixture of chlorine and hydrogen, the initial reaction should use up the three types of molecules in the proportions  $1 : 10^9 : 10^{24}$ , and the hydrogen chloride formed should be almost entirely  $\text{HCl}^{37}$ . The experimental results, however, of applying this method were entirely negative.

In conclusion, it may be pointed out that the actual numerical results achieved by lengthy and laborious operations in the few successful attempts indicate very clearly that unless some entirely new means of attack is devised no serious practical disturbance of the constants of chemical combination need be anticipated in the immediate future.

*Artificial Disintegration of the Lighter Elements by the Collision of Swift  $\alpha$ -Particles.*

The remarkable results in this field obtained by Rutherford and Chadwick during the year 1921 have already been reported,<sup>58</sup> and a complete account of their work up to February 1922 will be found in Sir Ernest Rutherford's lecture before the Chemical Society.<sup>59</sup> In a more recent publication,<sup>60</sup> these results have been confirmed and extended. The nature of the particles ejected from the various elements during the bombardment by swift  $\alpha$ -particles has been directly investigated by measuring their deflexions in a magnetic field. The results show that in the cases of aluminium, phosphorus, and fluorine the particle ejected is a single positively

<sup>56</sup> *Proc. Camb. Phil. Soc.*, 1922, **21**, 45; *A.*, ii, 497.

<sup>57</sup> H. Hartley, A. O. Ponder, E. J. Bowen, and T. R. Merton, *Phil. Mag.*, 1922, [vi], **43**, 430; *A.*, ii, 280.

<sup>58</sup> *Ann. Rep.*, 1921, **18**, 31.

<sup>59</sup> *T.*, 1922, **121**, 400.

<sup>60</sup> Sir E. Rutherford and J. Chadwick, *Phil. Mag.*, 1922, [vi], **44**, 417; *A.*, ii, 682.

charged hydrogen nucleus, which is now regarded as being identical with the ultimate atom of positive electricity or proton. The same is also probably true of boron and sodium. The ranges of the protons ejected, in the forward and backward directions, from nitrogen, aluminium, boron, fluorine, sodium, and phosphorus have been more accurately determined. In all cases, the protons were ejected in all directions, and the maximum range in the backward direction was less than in the forward direction. The maximum ranges, in cm. of air, of the ejected protons, in the forward and backward directions, respectively, were found to be: boron, 58 and 38; nitrogen, 40 and 18; fluorine, 65 and 48; sodium, 58 and 36; aluminium, 90 and 67; and phosphorus, 65 and 49. Only in the case of nitrogen was the maximum range in the backward direction much less than that of the protons produced by the bombardment of hydrogen itself. No protons of range greater than 30 cm. of air, in a forward direction, were ejected from either lithium or glucinum, and there is no evidence of the ejection of long-range protons from magnesium, silicon, or chlorine. It is a very remarkable thing that of the series of elements from hydrogen to potassium so far examined the active elements (those from which high-speed protons can be ejected) are odd-numbered in the order of atomic number in sequence 5, 7, 9, 11, 13, 15. The atomic masses of these active elements are all expressed by  $4n + a$ , where  $n$  is a whole number and  $a = 3$  for all except nitrogen and the lighter isotope of boron, for which  $a = 2$ . With the one exception of boron, all are simple elements.

It is evident from these results that the nuclei of even light elements are very complex structures. The effects mentioned above are best explained by the view that the fragile nuclei of the active elements have a different proton-electron structure from those not exhibiting disintegration, and that their fragility is due to the presence of what may be called "planetary" protons less firmly bound than their fellows and probably rotating in orbits of nuclear dimensions. The fact that chlorine and the heavier elements do not break up may be ascribed to their nuclear charge being so high that the  $\alpha$ -particle never makes a close enough collision to effect disintegration. Disintegration is clearly akin to ionisation, since in each case a unit electric charge is torn violently away from the atom, but beyond this the parallel ceases. In the case of ionisation the field of force round the atom is of a sign which attracts the electron dislodged, or any other electron, and extends indefinitely in all directions, so that the atom is sure to regain its neutral form very rapidly. On the other hand, in disintegration, any field of force tending to regain the proton lost is confined to nuclear dimensions



and in addition is surrounded indefinitely in all directions by a field of force repelling such a positive charge. The effect of ionisation is therefore transitory, whilst that of disintegration is permanent, and it is not unreasonable to speculate that when a proton is dislodged from an atom of sodium ( $\text{Na}^{23}$ ) there results an atom of neon ( $\text{Ne}^{22}$ ) which, as soon as it has lost its excess electron, will be indistinguishable in any way from any other atom of  $\text{Ne}^{22}$ . Even if the actual effect is not so simple as this, there can be no doubt that alchemical transmutation has been achieved. An attempt made by Wyckoff<sup>61</sup> to effect transmutation by bombardment of lithium salts by a stream of electrons, in the hope of introducing one or two into the nuclei of the lithium atoms, was unsuccessful. The claim put forward by Wendt and Irion<sup>62</sup> that tungsten is decomposed and partly transmuted into helium when, in the form of a fine wire, it is electrically deflagrated at a very high temperature, appears so excessively improbable that it may be safely left for further confirmation.

#### *$\alpha$ -Rays.*

The range of  $\alpha$ -rays in solids and liquids has been measured by Trautenberg. In the first case,<sup>63</sup> a small-angled wedge of the material was arranged with its lower face parallel to, and at a distance of a few millimetres from, a plane surface activated by means of radium-*C*. The upper face of the wedge was in contact with a zinc sulphide screen. The range of the  $\alpha$ -rays in the solid was determined by observing the distance of the line of demarcation between the light and dark regions of the screen from the angle of the wedge. Correction was made for the thickness of air traversed.  $\beta$ -Radiation was eliminated by a powerful magnetic field. The following results were obtained for the respective ranges, expressed in  $10^{-4}$  cm., in the various elements stated: lithium, 129.1; magnesium, 57.8; aluminium, 40.6; calcium, 78.8; iron, 18.7; nickel, 18.4; copper, 18.3; zinc, 22.8; silver, 19.2; cadmium, 24.2; tin, 29.4; platinum, 12.8; gold, 14.0; thallium, 23.3; lead, 24.1. These results can be correlated by a formula, but helium and lithium do not satisfy this relation; this discrepancy is ascribed to the production of secondary  $\alpha$ -radiation.

In the case of liquids,<sup>64</sup> the range was measured by immersing the activated plate in the liquid and lowering the screen towards it until it just fluoresced; the thickness of the liquid was then

<sup>61</sup> *Science*, 1922, 55, 130; *A.*, ii, 642.

<sup>62</sup> *J. Amer. Chem. Soc.*, 1922, 44, 1887; *A.*, ii, 773.

<sup>63</sup> *Z. Physik*, 1920, 2, 268; *A.*, 1921, ii, 148.

<sup>64</sup> H. R. von Trautenberg and K. Philipp, *Physikal. Z.*, 1921, 22, 587; *A.*, ii, 12.

measured with a horizontal microscope. The range in water was found to be  $60\mu$ . Gases were investigated by passing the beam of rays parallel to the sides of a glass wedge, containing the gas, and placing in their path a screen at a small angle with the horizontal. As in the case of solids, the range was deduced from the boundary of dark and light on the screen. They found that the stopping power of gases varies as the square root of the atomic number, but is not strictly additive in the case of compounds.

The luminous path of  $\alpha$ -rays in crystals has been observed by Geiger and Werner.<sup>65</sup> A thin, highly polished section of willemite was arranged in the field of a microscope so that the  $\alpha$ -rays of polonium should strike it at a small angle. Luminous lines, 0.03 mm. long, were seen. These represent the path of the  $\alpha$ -ray in the crystal and show that the number of centres is extremely large, and in the case of a perfect crystal sufficient to ensure a scintillation for every  $\alpha$ -particle hitting the crystal.

Some exceedingly important observations on the collisions between  $\alpha$ -particles and hydrogen nuclei have been made by Chadwick and Bieler.<sup>66</sup> The angular distribution of these nuclei, or protons, projected by  $\alpha$ -particles of mean range 6.6 cm., has been determined up to an angle of  $66^\circ$ . The distribution for  $\alpha$ -rays of mean ranges 8.2, 4.3, and 2.9 cm. has been obtained over a smaller range of angle. The number of protons projected within these small angles by  $\alpha$ -rays of high velocity is greatly in excess of that given by forces varying as the inverse square of the distance between the centres of the two nuclei. The manner in which the number of protons projected varies with the velocity of the rays has been observed over a wide range. For rays of high velocity this variation is in the opposite direction to that given by the inverse square law; for those of range less than 2 cm. the collision relation is about the same as that expected from the inverse square law. The experimental collision relation is compared with those calculated by Darwin for various models of the particle, and the conclusion is drawn that the  $\alpha$ -particle behaves in these collisions as an elastic oblate spheroid of semi-axes about  $8 \times 10^{-13}$  and  $4 \times 10^{-13}$  cm., moving in the direction of its minor axis. Outside this surface the force varies approximately as the inverse square of the distance from the centre of the spheroid.

Slater<sup>67</sup> has investigated the hard  $\gamma$ -radiation which is emitted when  $\alpha$ -particles from radium emanation impinge on metals such as lead and tin. The radiation differs but little with change of

<sup>65</sup> *Z. Physik*, 1921, 8, 191; *A.*, ii, 183.

<sup>66</sup> *Phil. Mag.*, 1921, [vi], 42, 923; *A.*, ii, 12.

<sup>67</sup> *Ibid.*, 904; *A.*, ii, 13.

atomic number. The absorption coefficients in lead are  $1.8^{-1}$  cm. for lead and  $2.1^{-1}$  cm. for tin. The intensity obtained is small, and is about 50 per cent. greater for lead than for tin. It appears to be emitted fairly uniformly in all directions, but differs in all other respects from the characteristic radiations, and is probably emitted from the nuclei of the atoms in the radiator after direct collision with the  $\alpha$ -particles. Shenstone<sup>68</sup> has attempted to detect the induced radioactivity resulting from  $\alpha$ -ray bombardment. He shows that the violent dismemberment of a molecule by an  $\alpha$ -particle does not give rise to unstable nuclei, capable of emitting mass particles of a range greater than 2.0 mm. Also no cumulative effect is observable after a heavy bombardment by the  $\alpha$ -particles. These negative results do not preclude the possibility of disintegrations taking place which involve the emission of  $\beta$ -particles or  $\gamma$ -radiation.

The velocity of  $\alpha$ -rays from polonium has been measured directly by Mlle Irene Curie<sup>69</sup> by means of a magnetic deviation method. A value of  $1.593 \times 10^9$  cm. per second is obtained and the ratio of the emission velocities of the  $\alpha$ -rays of polonium compared with those of radium-*C* is accordingly 0.829, which is in excellent agreement with the ratio 0.826 obtained from the cube roots of their penetrating powers. An interesting point is raised by Henderson<sup>70</sup> in a communication entitled " $\alpha$ -Particles as Detonators." If it is considered that when an  $\alpha$ -particle passes through matter the matter in its proximity is momentarily raised to a high temperature, the detonation of certain unstable substances would be expected to take place on exposure to the action of these particles. Air-dried nitrogen iodide is detonated in this way. The detonation is not caused by the first  $\alpha$ -particle which happens to strike the substance, but appears to be a probability effect. The same investigator<sup>71</sup> has measured the ionisation curves of  $\alpha$ -particles from radium-*C*, thorium-*C*<sub>1</sub>, and thorium-*C*<sub>2</sub> in air, particular attention being directed to the end portions. The greater part of each curve is approximately a straight line. The gradual flattening of the curve at the end of the range can be accounted for by small variations in the ranges of individual  $\alpha$ -particles. He suggests that an extrapolated range is more suitable than the usual definition. The extrapolated range in air at 0° is 6.592 cm. for radium-*C*, 4.529 cm. for thorium-*C*<sub>1</sub>, and 8.167 cm. for thorium-*C*<sub>2</sub>.

<sup>68</sup> *Phil. Mag.*, 1922, [vi], 43, 938; *A.*, ii, 377.

<sup>69</sup> *Compt. rend.*, 1922, 175, 220; *A.*, ii, 606.

<sup>70</sup> *Nature*, 1922, 109, 749; *A.*, ii, 606.

<sup>71</sup> *Phil. Mag.*, 1921, [vi], 42, 538; *A.*, 1921, ii, 617.

*The Scattering of  $\beta$ -Rays.*

Geiger and Bothe<sup>72</sup> have measured the scattering of  $\beta$ -rays by thin metal sheets (*a*) in the regions of small scattering angle ( $\phi = 15^\circ$  or less) and (*b*) in the regions of large scattering angle ( $\phi = 60^\circ$  or more). They show that there is a fundamental difference between the two types of scattering. In the region of smaller angles, the observed angle is produced by the superposition of many individual small scattering angles through which the  $\beta$ -ray is bent as it passes the individual atoms (multiple scattering), whilst in the region of large angles the superposition plays a subordinate rôle; each scattering angle is produced by a single collision when the path of the electron lies very close to the nucleus of the atom collided with (individual scattering). In the case of rays from radium- $(B + C)$ , they show that for the very thinnest layers the scattering is less than that demanded by the square root law, but that for thicker layers this law is confirmed.

The same phenomenon has been very completely investigated by Crowther and Schonland.<sup>73</sup> A source of radium emanation of an initial activity equivalent to that of 45 mg. of radium was employed and the scattering of the  $\beta$ -rays caused by foils of gold, silver, copper, aluminium, and carbon was measured over ranges of both large and small angles. In the experiments on the relation between the transmitted radiation and the thickness of the scattering material, they conclude that this is a linear one for thin foils. If  $t_m$  is the thickness of material sufficient to cut down the radiation to one-half its initial intensity, their results may be summarised by stating that, for light elements such as carbon and aluminium, the scattering as measured by  $\phi/\sqrt{t_m}$  is independent of  $\phi$  over the whole range of the angles investigated ( $4^\circ$  to  $18^\circ$ ), but has a value which is nearly twice that to be expected on the current theories of the effect. On the other hand, for heavy elements like gold or platinum, the scattering for very small values of  $\phi$  approximates closely to that to be expected from theoretical considerations, but increases rapidly with the angle, until for angles of  $18^\circ$  it is in agreement with the larger scattering shown by the lighter elements at all angles measured.

Their method of viewing the data strongly suggests that some change is required in the present theory when the distance between the path of the  $\beta$ -particle and the deflecting particle is less than a certain critical value.

Glasson<sup>74</sup> has tabulated values of the atomic absorption,

<sup>72</sup> *Physikal. Z.*, 1921, 22, 585; *A.*, ii, 13.

<sup>73</sup> *Proc. Roy. Soc.*, 1922, [A], 100, 526.

<sup>74</sup> *Phil. Mag.*, 1922, [vi], 43, 393; *A.*, ii, 183.

$\alpha = \alpha A/D$ , and the atomic scattering,  $b = \beta A/D$  (where  $A$  is the atomic weight,  $D$  the density, and  $\alpha$  and  $\beta$  are the coefficients of absorption and of scattering, respectively, for  $\beta$ -rays) of the elements, and has discovered two interesting relations. He finds that the values of  $\alpha$  are approximately constant for elements in the same period of the periodic system. Thus for Mg, Al,  $\alpha = 89$ ; for Fe, Co, Ni, Cu, Zn,  $\alpha = 172$ —196; for Pd, Ag, Sn,  $\alpha = 260$ —268; and for Pt, Pb, Au, Bi,  $\alpha = 348$ —372. These figures are in the ratio 1 : 2 : 3 : 4, so that it seems likely that the value of  $\alpha$  is a periodic function of the atomic number. The value of  $b$  increases with atomic number and is approximately represented by the expression  $b = 0.36 \times N^{2.09}$ .

*$\beta$ -Rays,  $\gamma$ -Rays, and the Structure of the Nucleus.*

The comparative lack of experimental data connected with the structure of the nucleus gives a very free field to speculative theory on that subject. The nucleus model put forward by Meitner<sup>75</sup> has been discussed by Neuberger, Valeras, and its originator in a number of papers of a speculative and controversial nature.<sup>76</sup> Other types of models are put forward by Gehreke,<sup>77</sup> Chwolson,<sup>78</sup> and Stewart.<sup>79</sup>

Ellis<sup>80</sup> has examined the magnetic spectrum of the  $\beta$ -rays excited by the  $\gamma$ -rays of radium-*B* in uranium, lead, platinum, tungsten, and barium. He shows that the main lines are formed by electrons ejected from the *K*-rings of these elements by definite  $\gamma$ -rays, each type of  $\gamma$ -ray being characterised by a certain energy. In a later paper,<sup>81</sup> he develops a method, based on the quantum theory, by which the wave-length of  $\gamma$ -rays, too short to be measured by the crystal method, can be determined, and applies this to the cases of the  $\gamma$ -rays of radium-*B*, radium-*C*, and thorium-*D*. The method consists in the determination of the energies of the different lines in the natural  $\beta$ -ray spectrum of the element in question, and the energy of the corresponding line in the excited spectra of substances of neighbouring atomic number. The numerical results obtained support the view that the  $\gamma$ -rays are emitted from the nucleus. They also suggest that the quantum theory is applicable to the nucleus, and a part, at least, of the structure of the nucleus is expressible in terms of stationary states.

<sup>75</sup> *Z. Physik*, 1921, **4**, 146; *A.*, ii, 293.

<sup>76</sup> *A.*, ii, 107, 183, 185, 416, 702, 732, 733.

<sup>77</sup> *A.*, 1921, ii, 323.

<sup>78</sup> *A.*, ii, 209.

<sup>79</sup> *A.*, ii, 277.

<sup>80</sup> *Proc. Roy. Soc.*, 1921, [*A*], **99**, 261; *A.*, 1921, ii, 422.

<sup>81</sup> C. D. Ellis, *ibid.*, 1922, [*A*], **101**, 1; *A.*, ii, 339.

Meitner,<sup>82</sup> on the other hand, although admitting that the origin of the  $\gamma$ -rays is the nucleus itself, gives an entirely different explanation of Ellis's results on the basis of her nucleus model, developed by the application of the quantum theory by Smekal.<sup>83</sup> The Meitner-Smekal theory supposes that the primary cause of  $\gamma$ -rays are  $\beta$ -rays of definite energies, and on it the well-known continuous  $\beta$ -ray spectrum must be considered to be entirely adventitious and produced under experimental conditions by some such agency as scattering. Ellis's explanation, which is more in accord with the older work of Chadwick,<sup>84</sup> is that the disintegration electrons form the continuous spectrum. The homogeneous groups are considered to be entirely secondary in origin and due to the conversion of  $\gamma$ -rays in the electronic structure of the radioactive atom, these  $\gamma$ -rays being emitted from the nucleus during the disintegration.<sup>85</sup> Chadwick and Ellis<sup>86</sup> have made a preliminary measurement of the intensity distribution in  $\beta$ -ray spectra of radium-*B* and radium-*C*, under conditions which enabled scattering effects to be eliminated or corrected for. Their results show that in each case by far the greater part of the intensity is in the continuous spectrum, a fact exceedingly difficult to explain on the Meitner-Smekal theory, and are generally in strong support of that put forward by Ellis.

The work on  $\beta$ -rays caused by  $\gamma$ -rays is still in progress and has already raised points of very great interest. It suggests that the origin of some of the electrons forming the  $\beta$ -rays must be inside the *K*-ring and therefore within the nucleus itself, and that these electrons have energies corresponding with definite quantum levels, just as the ordinary planetary electrons outside are known to have. Now the effect of an isotopic difference in the structure of nuclei may be expected to have an enormously greater effect on  $\beta$ -ray spectra caused by nuclear electrons than it would have on *X*-ray or ordinary light spectra caused by planetary electrons. Multiple lines observed already give evidence that some of the heavy elements examined are mixtures of isotopes, but, unfortunately, none of these has yet been analysed by the mass-spectrograph. It is also clear that if an electron is dislodged from the nucleus by the agency of a  $\gamma$ -ray produced in the nucleus itself, it is just possible that the same effect could be produced, and transmutation effected, by a  $\gamma$ -ray from an exterior source. Assuming that the emission of

<sup>82</sup> *Z. Physik*, 1922, **9**, 131; *A.*, ii, 416.

<sup>83</sup> *Ibid.*, 1922, **10**, 275.

<sup>84</sup> *Verh. deut. Physikal. Ges.*, 1914, **16**, 383.

<sup>85</sup> C. D. Ellis, *Proc. Camb. Phil. Soc.*, 1922, **21**, 121; *A.*, ii, 466.

<sup>86</sup> *Ibid.*, p. 274.

$\gamma$ -rays may precede the process of disintegration, Hevesy<sup>87</sup> shows that if the nucleus could take up the energy of a  $\gamma$ -ray from an external source it should change its stability and therefore its rate of disintegration. He has experimented with uranium in radioactive equilibrium with uranium-*X*, and with radium-*D* in equilibrium with radium-*E*, but has failed to detect a measurable change in the  $\beta$ -radiation in either case.

### *Thorium.*

*Long-range Particles from Thorium-C.*—In the disintegration of thorium-*C* a small number of particles with the long range of 11.3 cm. are expelled.<sup>88</sup> As there was a possibility that these had originated by collisions of the  $\alpha$ -particles with the oxygen of the mica absorbing screen, the phenomena were re-examined with screens of aluminium as well as mica.<sup>89</sup> The same results were obtained in both cases. The ratio of the total number of particles with ranges exceeding 8.6 cm. to the total number of  $\alpha$ -particles (ranges 5.0 and 8.6 cm.) is 1 to 11,000. At least 90 per cent. of the long-range particles originate in the active deposit. Measurement of the deflexion of these particles in a magnetic field showed that they were ordinary  $\alpha$ -particles of mass 4. There is no information as to their source. It may be that thorium-*C* may break up in two ways with the emission of rays of ranges 8.6 and 11.3 cm., or that 1 in 11,000 of the atoms of thorium-*C* breaks up directly with emission of these very swift  $\alpha$ -particles. The resulting product would have an atomic number 81, and would be an isotope of thallium with atomic weight 208. The amount of this thallium found in thorium minerals should be about 0.00004 per cent.

The number and the range of the recoil atoms of thorium-*C* and thorium-*C'* have been investigated by Kolhorster.<sup>90</sup> Aluminium foil, activated by a mesothorium preparation, was used as a source of the radiation. It is concluded that a recoil atom results from each atom of thorium-*C* and thorium-*C'* transformed by the emission of an  $\alpha$ -ray. The average ranges found in hydrogen were 0.55 mm. and 0.96 mm., respectively, corresponding with ranges of 0.129 mm. and 0.224 mm. in air at 15° and 760 mm.

A determination of the number of  $\alpha$ -particles per second emitted by thorium-*C* of known  $\gamma$ -ray activity has been made by Shenstone and Schlundt.<sup>91</sup> The  $\alpha$ -particles were counted by the wheel method

<sup>87</sup> *Nature*, 1922, 110, 216; *A.*, ii, 608.

<sup>88</sup> Sir E. Rutherford, *Phil. Mag.*, 1921, [vi], 41, 570; *A.*, 1921, ii, 293.

<sup>89</sup> A. B. Wood, *ibid.*, p. 575; *A.*, 1921, ii, 294.

<sup>90</sup> *Z. Physik*, 1920, 2, 257; *A.*, 1921, ii, 149.

<sup>91</sup> *Phil. Mag.*, 1922, [vi], 43, 1038; *A.*, ii, 417.

devised by Rutherford, and accurate  $\gamma$ -ray measurements were made at the same time as the counts. Counts made with thorium-*C* and radium-*C* showed that the ratio of their  $\alpha$ -ray activities for equal  $\gamma$ -ray activities is not independent of the thickness of the wall of the  $\gamma$ -ray electroscope.

The volatility of a radioactive product, deposited on metal, has been examined in the case of thorium-*B* and thorium-*C*, deposited on gold, platinum, and palladium.<sup>92</sup> A discontinuity at about 760° is put down to the occurrence of thorium-*C* oxide stable at this temperature.

Strong<sup>93</sup> has made a careful series of fractionations of a mixture containing radium and mesothorium obtained during the process of extraction from barium compounds. No separation whatever could be detected, from which it is concluded that radium and mesothorium are true isotopes.

#### *Uranium and Actinium.*

Adams<sup>94</sup> points out that Piccard's assumption<sup>95</sup> that the actinium series is derived neither from uranium-I nor from uranium-II does not require the identity of the periods of the first and the third. A hypothetical isotope of protoactinium (ekatantalum or uranium-*Z*) is assumed as the parent of actinuranium by a  $\beta$ -ray transformation. He assigns to this element an atomic weight 235, corresponding with protoactinium 231, actinium 227, and actinium lead 207, and points out that the last value agrees well with Hönigschmid's value of 206.05 for the atomic weight of uranium lead containing about 3 per cent. of actinium lead.

Meyer<sup>96</sup> calculates the half-life period of actinium to be about sixteen and a half years, and the transformation ratio of the actinium to the uranium family to be 4.2 per cent. Hahn and Meitner<sup>97</sup> consider this value to be 25 per cent. too high, and prefer their own value,  $3 \pm 0.3$  per cent. They consider that Meyer's preparation probably contained 1—2 per cent. of ionium, which would explain the difference. The same workers,<sup>98</sup> by separation of the protoactinium from uranium of approximately known age and measurement of its activity in comparison with that of uranium, have been able to estimate its half-life period as about 12,000 years. This value is the result of three concordant experiments and is

<sup>92</sup> S. Loria, *Krakauer Anzeiger*, 1917, 260; *A.*, 1921, ii, 294.

<sup>93</sup> *J. Amer. Chem. Soc.*, 1921, 43, 440; *A.*, 1921, ii, 294.

<sup>94</sup> *Ibid.*, 1920, 42, 2205; *A.*, 1921, ii, 8.

<sup>95</sup> *A.*, 1918, ii, 6.

<sup>96</sup> *Wien. Anzeiger*, 1920, 133; *A.*, 1921, ii, 8.

<sup>97</sup> *Z. Physik*, 1921, 8, 202; *A.*, ii, 185.

<sup>98</sup> *Ber.*, 1921, 54, [B], 69; *A.*, 1921, ii, 150.



to be regarded as the lower limit. It is thus possible to calculate the protoactinium content of uranium minerals, which is expressed by the figure 72 mg. of protoactinium to one ton of uranium; the corresponding figure for radium is 330 mg.

*New Radioactive Substances in Uranium.*—Hahn<sup>99</sup> describes a new radioactive substance present in ordinary uranium salts possessing the chemical properties of protoactinium. It emits  $\beta$ -radiations and has a half-life period of six to seven hours. The radiations are highly complex; within the limits examined, the halving thickness increases from 0.014 to 0.12 mm. of aluminium. Under the prescribed conditions, the intensity of radiation of the new substance is only about 0.25 per cent. of that of uranium- $X$  (uranium- $X_1$  + uranium- $X_2$ ), obtained from the same quantity of uranium. The parent substance can only be uranium- $X_1$  or a new uranium- $X_1$  isotope of similar life period. In the former case, uranium- $X_1$  suffers a dual degradation of a type not yet observed. In the latter case, it is probable that a new uranium degradation series exists which has a small intensity of radiation and the individual members of which can be arranged as isotopes in the known uranium-radium series. Until the parentage of the new substance is definitely established, the author proposes to designate it "uranium- $Z$ ." Neuburger<sup>1</sup> suggests possible types of disintegration in the uranium-radium series to account for the occurrence of the new uranium- $Z$ . Hahn,<sup>2</sup> however, rejects the transformations suggested by Neuburger as improbable.

Piccard and Stahel<sup>3</sup> have repeatedly measured the  $\beta$ -radiation of a quantity of uranium- $X$  for a prolonged period. They show that in addition to the hard  $\beta$ -radiation of uranium- $X$ , there is a soft radiation which with increasing age of the preparation decreases more and more slowly; this indicates the presence of a substance of longer life than uranium- $X$ . They name this provisionally "uranium- $V$ ." It has a half-life period of about forty-eight days, its  $\beta$ -radiation is half absorbed by an aluminium sheet 0.0003 mm. thick, and it may be a member of the actinium series. Hahn<sup>4</sup> has determined the decrease in activity of a number of uranium- $X$  preparations to test these observations, but has found no evidence of the existence of uranium- $V$ .

F. W. ASTON.

<sup>99</sup> *Ber.*, 1921, **54**, [B], 1131; *A.*, 1921, ii, 478.

<sup>1</sup> *Naturwiss.*, 1921, **9**, 235; *A.*, 1921, ii, 479.

<sup>2</sup> *Ibid.*, 236; *A.*, 1921, ii, 479.

<sup>3</sup> *Physikal. Z.*, 1922, **23**, 1; *A.*, ii, 185.

<sup>4</sup> *Ibid.*, 146; *A.*, ii, 340.

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## ERRATUM.

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Page	Line	
70	11	for "reduction" read "dehydration."